THE MANUFACTURE OF SULPHURIC ACID (CONTACT PROCESS)

BY

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EDITOR'S PREFACE

THE first English edition of Lunge's *Sulphuric Acid and Alkali* appeared in 1879. Since that date the book has been revised and extended in subsequent editions until, with the companion volumes on *Coal Tar and Ammonia*, it extended to nine volumes, covering most of the heavy chemical industries of Britain. A supplementary volume on Sulphuric and Nitric Acids by Dr Lunge in 1917 marked the end of his long labours in this field, and he informed the publishers that he could no longer undertake the preparation of new editions. The mere compilation of the volumes which he wrote would be in itself a wonderful achievement, but Dr Lunge's place in the history of chemical industry is due still more to the fact that he played a leading part in the discoveries and improvements which built up the industries of which he wrote.

By a curious coincidence, the end of Dr Lunge's long literary labours came just as the processes which he originally described died out. The Hargreaves process has gone, in this country at least; the Leblanc process is dying, if not actually dead already; even the chamber process for sulphuric acid has now a competitor that threatens to become a rival.

The volumes written by Dr Lunge have escaped a common criticism of factory managers that books give only an outline of a manufacturing process; indeed the only criticism has been that Dr Lunge's books gave almost too much detail. It may, however, be realised how important is a detail relating to a matter involving a possible saving of only one-tenth of one per cent., when it is pointed out that this small economy in the

manufacture of sulphuric acid would mean a saving of thousands of pounds, since the value of the sulphuric acid manufactured annually in Great Britain alone amounts to several million pounds.

Each new edition of this series has been an expansion and extension of that which preceded it, fuller treatment being accorded to subsidiary manufactures as they increased in commercial importance, until the name *Sulphuric Acid and Alkali* became a cover for what was practically an encyclopedia of the heavy chemical industries.

The last arrangement into volumes and parts was largely fortuitous, having arisen from uneven growth of knowledge and commercial development in different branches, and as this appeared to be a favourable opportunity for instituting a new arrangement, it was decided to sub-divide the work into sections more in accord with modern developments. The last few years have brought with them so many changes in the chemical industries that the revision required in most of the volumes will involve such drastic recasting that the new edition will be more a new book than a revised edition.

It is doubtful if any one man could take up Dr Lunge's task of describing adequately all the industries now dealt with in these volumes, and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author who is responsible for that volume, and is given a wide discretion in his treatment of the subject.

The editor trusts that these united efforts will produce a new edition worthy of the great tradition which Dr Lunge has established.

The editor will be pleased to consider for publication in this series any manuscripts or original work on this or allied subjects.

A. C. C.

LIVERPOOL.

AUTHOR'S PREFACE

THERE is nothing to be gained in the long run, and there is much that may be lost, by distinguishing too sharply between the technical and scientific aspects of a chemical process of manufacture. I have tried to treat the subject in such a way that the distinction is marked as little as possible, and that neither side suffers at the expense of the other.

The technical aspect is the more difficult of the two to deal with, for the Contact Process is only now emerging from the secrecy which has so long obscured much of its actual operation. The lines along which development will move may now be discerned. I hope this book will escape the reproach that has often met publications on this subject—that no plant or process was ever described until it had proved ineffective or had fallen out of date—but until a Process has reached finality, there must always be certain variations which remain known only to a few.

In regard to the scientific aspect, secrecy is not so great a hindrance. To the technologist who deals with acids the data on which the Process is based are probably of more use than descriptions of plant and methods which he may already know quite well enough. Considerable pains have been taken, therefore, to make these data complete and accurate, and to pass them, together with any significant theories to which they give rise, under critical review.

Forming as it undoubtedly does one of the most clearly marked sequences of operation in chemical engineering, the Contact Process lends itself well to the discussion, from a point

of view which may be technical and scientific at once, of each operation separately. Descriptions of plants as a whole have been deferred until this treatment is complete. In dealing with routine calculations full use has been made of nomographic charts, nearly all of which have been devised specially for the subject in hand.

I am greatly indebted to Mr W. Rintoul, O.B.E., F.I.C., for his interest and encouragement during the publication; to Dr J. W. M'David, Chief Superintendent of the Acids Department at Ardeer, for reading the proofs and giving much helpful advice; to Mr H. R. Neech, F.I.C., for contributing useful information, and to many others who in lesser degree have done the same. Acknowledgments are due to the Department of Scientific and Industrial Research and to Mr W. Macfab C.B.E., F.I.C., for permitting the reproduction (from Technical Record of Explosives Supply, No. 5) of the folding plates of the Grillo and Mannheim plants.

F. D. MILES.

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THE MANUFACTURE OF SULPHURIC ACID (CONTACT PROCESS)

CHAPTER I

THE HISTORY OF THE MANUFACTURE OF FUMING SULPHURIC ACID

HISTORICAL SKETCH OF THE DEVELOPMENT OF THE CONTACT PROCESS

THE Contact Process for manufacturing sulphuric acid is one of the foremost achievements of technical chemists. Originating in the discovery of Peregrine Phillips, a vinegar manufacturer of Bristol, in 1831, this application of a simple reaction between two gases has passed through many stages, in which, at different times, hope, doubt, confusion, and at last the satisfaction of success have filled the minds and influenced the energies of three generations of workers. To recount this development is to demonstrate in a most striking way that the progress of technology has often been independent of advances in pure science, and has owed little to them. The worker in technical science acquires knowledge, mainly by experience, to serve certain definite ends; the purely scientific investigator seeks knowledge for its own sake. It is therefore unlikely that phenomena which interest the one will interest the other at the same time. Hardly any chemical reaction between gases has been of greater interest from the purely chemical point of view—as an example of the principles involved in all gas-reactions, or as a starting point for investigations in the mysterious field of catalysis. Such opportunities as these

have not been altogether lost; from a scientific point of view the reaction is now well known, and practice is the richer for being given many and various data; yet it is fair to say that the application of the newer principles of chemistry was never made when it was most required, and that even now there are many aspects of the reaction and properties of the substances involved, which have been only incompletely examined.

For many years the discovery of the mechanism of gas reactions, and the achievements in the technical production and use of gases, were fields of knowledge separate from each other. But in the end the barriers dividing knowledge are broken down, and we may hope to have, in regard to the Contact Process in both technical and scientific aspects, a body of information which, from every point of view, is equal to that applying to any other chemical change.

In his specification, No. 6096 of 1831, for "certain improvements in manufacturing sulphuric acid, commonly called oil of vitriol," Peregrine Phillips describes the method of manufacture in use in his day. Sulphur and saltpetre, either mixed together in large leaden chambers, or separately in ovens, were burnt with the production of sulphur dioxide and nitrous acid. The sulphur dioxide was then converted *gradually* into sulphuric acid "by the agency of nitrous gas united with oxygen from the atmospheric air in the chamber, or from that liberated from the saltpetre." To continue in his own words: "The first improvement then, which I propose to effect is, an *instantaneous* union of the sulphurous acid gas with the oxygen of the atmosphere, and thereby to save the constant expense of saltpetre, and also the great outlay of capital in the chambers by the gradual conversion of the sulphurous acid into the sulphuric acid." This was to be done by "drawing the gases" in proper proportions by the "action of an air-pump, or by other mechanical means through an ignited tube or tubes of platina, porcelain, or any other material not acted on when heated by the sulphurous acid gas. In the said tube or tubes I place platina wire or platina in a finely divided state, and I heat them to a strong yellow heat, by preference in the chamber of a reverberatory furnace; and I do affirm that sulphurous acid gas being made to pass with a sufficient supply of air through tubes as

described, properly heated and managed, will be instantly converted into sulphuric acid gas, which will be rapidly absorbed as soon as it comes into contact with water. . . . The relative proportions of sulphurous acid gas and air are regulated by the size and working of the air-pump, which must pump at least eighty-five cubic feet of air for each pound of sulphur consumed."

The expression "strong yellow heat" is interesting. Phillips' second improvement was to consist in the absorption of the "sulphuric acid gas" in a tower 8 ft. wide by 30 ft. high—a prototype of the modern absorption tower. It was to be packed with pebbles nearly to the top, and on the surface of the packing was to be placed a perforated lead plate. A leaden pump was to maintain acid or water in circulation over this tower. No hint is given that the absorption in water might give trouble, or fail altogether.

This patent clearly describes the fundamental feature of the Contact Process as it is now known. The furthest advances which have been made in practical experience or in scientific knowledge, although they have changed and elaborated the process in many ways, have not changed it beyond the limits of this early conception. To Peregrine Phillips, of whom no other record appears in the history of either academic or technical science, belongs the credit of making the original scientific discovery, and of realising its possible commercial value.

The first observation of a "contact" reaction seems to have been made by Davy in 1817. Heated platinum wire introduced into a mixture of oxygen or air with hydrogen, carbon monoxide, ethylene, or cyanogen becomes hotter and finally glows, the gaseous mixture being rapidly burnt. Edmund Davy, in 1820, found that platinum black was very active in this way. In 1822 Döbereiner found that the residue produced by igniting ammonium-platinichloride caused the combustion of the alcohol with which it was moistened, and in 1823 that a current of hydrogen in air can be ignited by the contact action of this kind of platinum. The union of sulphur dioxide and oxygen was therefore of comparatively late discovery.

Almost immediately after the publication of Phillips' patent,

two German scientists repeated his experiments. Magnus[1] observed that a mixture of two volumes of sulphur dioxide and one of oxygen is gradually condensed to sulphuric acid, in the presence of water, but much more quickly in the presence of heated platinum, particularly of the spongy variety. Magnus also observed the formation of a little trioxide on passing the mixed gases through a tube containing broken glass, at a dull red heat. At the same time Döbereiner stated that he had succeeded in condensing a similar mixture to fuming sulphuric acid, by "hygroscopically moist" platinum black.

There is no doubt that from 1831 onwards the possibilities of Philips' patent were borne in mind by many chemists, and that, at frequent intervals, attempts were made to place the process on a technical basis, mainly with the intention of manufacturing the comparatively dilute acid already made in lead chambers. But more than forty years were to elapse before even an erroneous idea of the chemical principles involved was conceived, and after that innumerable difficulties connected with the employment of technical raw materials had to be faced and overcome by long and painstaking investigation.

Platinised asbestos was mentioned by Jullion for the first time in 1846 (B. P. 11425). He employed "asbestos covered or coated with platinum or other catalytic or contact substances" heated from 20° to 480° C., for various catalytic reactions. Among these were the oxidation of nitrogen oxides to nitric acid and the production of chlorine from hydrochloric acid. Although Jullion proposed to make sulphuric acid by oxidising sulphurous acid with chlorine, the contact process in its simple form was not among his proposals.

In 1847 it was reported that Schneider—a Belgian chemist—had carried out successful work on the manufacture of sulphuric acid and its concentration to 66° Bé. without lead chambers and without platinum, by a contact process. Descriptions of the process and drawings of the apparatus were published.[2] This excited great interest, and Schneider demonstrated his process to a number of persons, and later to a committee appointed to investigate it by the Académie des Sciences. Dumas, Pelouze, and Payen were members of the committee. Their report

[1] *Pogg. Ann.*, 1832, 24, 610.

[2] *Dingl. polyt. J.*, 56, 395; 89, 354

(written by Payen) states that the process had been demonstrated by means of a model—that in fact sulphuric acid had been made without nitric acid or a nitrate, with a yield approximating that of the usual manufacture. The "contact" material was pumice, but the method of preparing it was not revealed even to the committee. It was never known whether, as seems most likely, the pumice was platinised. The committee in reporting that they had seen Schneider make a full day's run with his apparatus and produce acid without using nitre, made the very natural remark that since they were unable to learn in what way the catalytic power had been imparted to the pumice, their finding in this respect must be limited to repeating Schneider's assertion that the treatment was by no means costly. This supposed invention received great publicity at the time but was not followed up. The most probable supposition is that Schneider was endeavouring to re-exploit Phillips' discovery of sixteen years before.

In 1835 Clément Desormes, writing to Schneider, expresses the prevailing hope of the time: "I am convinced that, in at most ten years, it will be possible to make sulphuric acid on the large scale from its constituents without lead chambers, nitric acid, or nitrates." The hope seemed justified; nothing but actual experience could reveal the manifold difficulties which lay ahead; the dawn of physical chemistry had not begun; the necessary knowledge of the mechanism of gas-reactions had still to be gathered.

As Knietsch has suggested, it is convenient to regard this as the first period in the development. It began with Phillips' invention and lasted just so long as attempts were made to exploit it, without adding anything to the knowledge of the contact reaction. Many other similar chemical changes had been discovered by Dulong, Thénard, Dumas, and others, and the idea had gained ground that the substances capable of "contact" action owed these properties to their porosity. The gases were condensed within the pores, and, occupying a very much diminished volume, the molecules were supposed to be much more nearly in contact, so that they could react more easily upon each other. In 1835 Berzelius classed these "contact" reactions with many others which had been observed in the domain of organic chemistry, *e.g.* the conversion of starch into

sugar, and with others such as the decomposition of hydrogen peroxide by various substances. Each of the reactions of this class occurs at the instance of a substance which itself appears to remain unchanged. Berzelius called these changes *catalyses* and attributed them to a "catalytic force" which could not be very clearly defined.

The second period in the History of the Contact Process saw but little progress. The aim remained the same—the replacement of lead chambers by simpler apparatus. Such advance as was made consisted in the recognition that many substances other than platinum were capable of functioning as contact materials. Laming, in 1848 (B. P. 12264), made a "*catalytic porous body*" *by boiling pumice-stone in* concentrated sulphuric acid, immersing in water containing a little ammonia, drying, and heating to about 300° with 1 per cent. of manganese peroxide. The "sulphureous gas" was to be "mixed with a due proportion of atmospheric air and a minute proportion of ammonia gas," and passed through columns of the catalyst, maintained at 300°. The trioxide was to be washed out from the columns with water. Much was hoped of this but no success resulted.

Blondeau, in the next year,[1] obtained some sulphuric acid by passing sulphur dioxide, air, and steam over argillaceous sand. He was led to this experiment by noting an observation of Boussingault's that sulphuric acid is to be found in some African rivers near which the gas from burning sulphur comes into contact with sand and schist. The sand used by Blondeau probably contained a sufficient amount of ferric oxide.

A more important contribution to the knowledge of the subject was made by Wöhler and Mahla in 1852.[2] They discovered that oxide of copper or chromium at a low red heat caused formation of thick fumes of sulphur trioxide when the constituent gases were passed over it. They confirmed the previous reports of the activity of platinum, and showed that copper was incapable of action, unless coated with oxide. Some experiments seem to have been made in pursuance of these discoveries, on a small technical scale,[3] but the results

[1] *Comptes rend.*, 1849, 29, 405.
[2] *Ann. Chim. Pharm.*, 1852, 81, 255.
[3] Wagner's *Jahresber.*, 1859, 144.

were disappointing. Wöhler and Mahla gave an explanation of the catalytic properties of these oxides, which was deemed satisfactory at the time and still possesses value. They demonstrated that oxide of iron, or oxide of copper, is capable of either reduction or oxidation under the conditions of the experiment, depending on trioxide or dioxide being in excess. Oxide of chromium is of course not included by this statement. They also showed that trioxide could be formed from gases which did not contain perceptible moisture. Although their work had no immediate result, it may be considered as the academic counterpart of the important Mannheim patents of more than forty years later.

Various patents were taken out soon after Wöhler and Mahla's work was published. Robb, in 1853 (B. Ps. 731 and 788), protected the manufacture of sulphuric acid by means of pyrites cinders as contact-mass. Thornthwaite, in 1854 (188, provisional), mentions the oxides of chromium and iron. Several oxides were mentioned by Trueman (B. P. 982) in 1854. Schmersal and Bouck (B. P. 183), in 1855, followed the same lines.

It is interesting to note that Deacon, whose well-known process for the manufacture of chlorine was invented about this time, protected the use of copper sulphate, among other substances, for the manufacture of sulphuric acid. In two respects he was far in advance of his time. He noticed that the reaction proceeded with more success if the air or oxygen were in excess, and that on this account the mass of air to be propelled would, in future processes, be greater than formerly. We now know, that to have present oxygen in excess of the molecular proportion, is one of the essentials of success. Deacon also observed that the gases issuing from the contact apparatus should not be cooled too suddenly, as such treatment made their condensation very difficult.

Various other patents about this time endeavoured to make use of silica. Hunt's proposal of 1853 (B. P. 1919) was apparently tried by Plattner at the *Müldener* works in Freiberg. The actual formation of trioxide must have been too small to be of any use. The predominance of British names throughout the early history of the process is very notable.

In this way closes the second period of the historical

development. No practical success had been attained. Attempts had all aimed at replacing the chamber process, mainly with a view to saving the cost of nitre. In these days this cost was much higher than at present, partly because nitre was itself costly, and partly because the recovery apparatus for nitric acid was either very crude or entirely lacking. Indeed, if other ends had been sought by inventors, and fuming acid had been made in any quantity, there would have been no outlet for it, because such small quantities as were required in Europe and elsewhere were supplied by the Bohemian works distilling it from the ferrous sulphate extracted from shale. Just for this reason inventors took no special precautions to exclude moisture from their catalysts, and indeed they often introduced water or steam on purpose. This caused the catalytic action to be very slow and imperfect. Nor was it sufficiently known at that time, and for many years later, what great importance lies in the removal of flue dust and other impurities; and last, though not least, the developments of chemical engineering were not sufficiently advanced to enable the results gained in the laboratory to be transferred to the works as readily as is the case at present. We shall not wonder at the length of the time required for the full development of Phillips' invention, if we consider that its working out was dependent on the general progress of chemical technology.

The first cause of slow development—the want of a market—was removed by the synthetic production of alizarine in the years 1868 to 1872. Other colouring matters rapidly followed, most of which required the preparation of sulphonic acids in intermediate stages. The demand for fuming sulphuric acid rapidly rose to such an extent that the Bohemian works, founded upon the exploitation of "copperas-slate," all of which then belonged to the firm of J. D. Starck, could hardly satisfy it, and the greatly enhanced price made this situation even more unbearable to the dye-manufacturers. Many chemists at that period turned their attention to the production of fuming sulphuric acid in other places and by other methods, either by carrying out the Bohemian process with some more suitable material than the Pilsen slates, or by applying one or more of the contact processes invented from the time of Phillips onw-

THIRD PERIOD—THE IDEAS OF CLEMENS WINKLER

The third period may be taken to have begun in 1875 with the publication of a paper by Clemens Winkler, professor in the School of Mining at Freiberg.[1] This paper is one of the two which have the greatest interest in regard to the history of the subject, and marked the beginning of most important developments. Winkler's experiments we now know to have been faulty. His conclusions contradicted the principles of mass action, but they were hailed with delight as an explanation of many previous failures and as an indication of the way to success. "The publication of Winkler's paper acted upon the industrial world like a sorcerer's wand upon pent-up spirits. The fatal spell resting upon the syntheses of sulphur trioxide seemed to be broken."

After dealing with the imperfections of the Bohemian Process and the attempts to make it more useful by reconverting the ferric oxide into sulphate with ordinary ("English") sulphuric acid, Winkler turned to discussion of the results previously obtained by contact action. Platinised asbestos is recommended in preference to platinised pumice or porcelain. In his experiments the gases were mixed and passed in a fairly rapid stream over platinised asbestos containing 8·5 per cent. of platinum, and maintained at a gentle glow. The gas mixture after conversion was absorbed in water and in sodium carbonate solution, and the conversion was deduced from the results of the analyses of the solutions. A mixture of pure dioxide and pure oxygen yielded 73·3 per cent. conversion, one of air and oxygen only 47·4 per cent., and the gas obtained by burning sulphur in air and containing 4 to 5 per cent. of dioxide, gave a yield of only 11·5 per cent. No indication was given of the ratio in which the two gases were mixed in the first two experiments.

Winkler then concluded: "From this it is apparent that the action of platinised asbestos and of all other contact substances is diminished in the same measure as the dilution of the sulphur dioxide by other indifferent gases is increased. Even sulphur dioxide and oxygen will naturally remain indifferent and act as diluents in so far as they are present in other than the stoichiometric ratio necessary for acid formation, that is, in so far as one gas or another is in excess."

[1] *Dingl. polyt. J.*, 1875, 218, 128. *See also* 1877, 223, 409.

To obtain the gases mixed in the required stoichiometric ratio, Winkler proposed to make use of the well-known decomposition undergone by sulphuric acid when heated. Sulphur dioxide and oxygen are formed, together with water which can readily be condensed, and the dry gases remaining can be passed over platinised asbestos at a low red-heat. He described, in the paper quoted, laboratory experiments in which about 78 per cent. of the acid used was decomposed, and about 74 per cent. of the products reunited by catalysis, and on this basis proposed that the manufacture should be carried out on a large scale. Such a yield would not now be considered satisfactory, but it should be borne in mind that the object in view—at that date—was not the production of ordinary, but of fuming acid, and that this commodity had risen enormously in price on account of the new demand for dye-production, while the world's supply was in the hands of a single firm.

The results obtained by Winkler in his experiments with the several gas mixtures are opposed to all experience, and it is difficult to imagine how he could have obtained them, or having obtained them, fail to find out from experience that they were wrong. This difficulty is increased by the absence of any statements of the compositions of his mixtures. His conclusions were contradicted by the Law of Mass Action, but this principle, enunciated in 1867 by Guldberg and Waage had, in 1875, received little attention from chemists in general, and was by no means widely accepted as a valid instrument of reasoning. Winkler's sophistries influenced general opinion for many years, and regret has often been expressed, for instance, by Ostwald in 1902, that so much time and trouble had been wasted.[1] Any chemist acquainted with Guldberg and Waage's Law, Ostwald states, could have shown the fallacy of the reasoning by pointing to the equation of the reaction. But for many years Winkler's results were quoted without criticism by all classes of chemists; the help which might have been given to generally received knowledge from the more modern principles of chemistry, failed altogether.

Nevertheless it seems reasonable to doubt whether much harm was done to the development of the process in a practical sense by this course of error, for no one whose interest in

[1] *Z. Elektrochem.*, 1902, 8, 154.

the matter was keen enough to make him repeat Winkler's experiments, or make others like them, can have failed to perceive their fallacy as Winkler himself very soon perceived it. Later, when he and others had turned their attention from the decomposition process to the more economical utilisation of the weaker gases from roasting-furnaces, the old statements were allowed to stand, forming, very probably, a useful distraction to general attention.

Winkler's process had a very considerable vogue, and a number of factories sprang up to exploit it. Great efforts were directed to overcoming the enormous difficulties of constructing plant in which sulphuric acid could be decomposed. The corrosive action is intense, and much pains and labour went to prove the impracticability of this operation alone. It has been pointed out that Winkler's omission to secure patents for his process in Germany reacted injuriously on investigation, for the protection of the process would have caused chemists to seek other fields, instead of confining themselves to this one, in which their efforts were foredoomed to failure

Almost on the same day that Winkler sent in his manuscript, an application for a British patent was lodged by W. S. Squire (B. P. 3278 of 18th September 1875). The process was very similar to Winkler's and was the common invention of W. S. Squire and Rudolf Messel, but the conclusion that a stoichiometric mixture was advisable was reached by much more valid reasoning. The two authors described their process in a paper read before the Chemical Society in the following year (20th April 1876). No record of this appears in the *Transactions*, but from information supplied by Messel (First Edition of this book), the following interesting points may be quoted. The invention had been actuated, like Winkler's, by the sudden rise in the price of fuming acid. They impregnated pumice with a mixture of platinum and ammonium chlorides, heated it to redness, and passed a mixture of air and dioxide over it. Dense clouds of trioxide were evolved, and their condensation was found possible only when the gases were originally present in the stoichiometric ratio. In the absence of foreign gases the condensation of liquid trioxide was "extremely perfect." The next step was to produce the gases on a commercial scale in the required ratio, and this they did

by decomposing sulphuric acid in a platinum still according to the well-known experiment of Deville, which Winkler had also repeated. The vapours from the still passed through a platinum tube maintained at nearly a white heat, and were then passed over platinised pumice. From 100 parts of acid nearly 70 parts of trioxide were obtained by condensation in Woulfe's bottles. In addition to platinum they also tried Wöhler and Mahla's mixture of the oxides of chromium and copper, made into pills with asbestos and heated to redness. Platinum, however, was found to be preferable, and a plant was erected at the Silvertown works (now Spencer, Chapman & Messel) capable of producing some tons of trioxide each week. They note that there was a loss of activity of the catalyst, due to the accumulation on it of such impurities as flue dust, when gases from the furnaces were used, and they point out that the method of producing the gases from sulphuric acid obviated this difficulty. This is one of the first records of loss of catalytic activity, but it is clear that "poisoning" in the sense now understood, *e.g.* by very minute amounts of arsenical matter, was not recognised by Squire and Messel. The fact that the gases employed for catalysis by platinum must be most carefully purified from arsenic and other deleterious substances was not fully recognised until many years after, when the patents taken out by the *Badische Anilin und Soda Fabrik* revealed the great attention which the inventors had paid to these impurities.

It has already been pointed out that although the process devised by Squire and Messel received patent protection in England, Winkler in Germany made no application for protection, so that in the latter country a considerable number of factories began the manufacture of fuming acid. The first acid made by the contact process on a commercial scale was that produced at the Kreuznach works by Emil Jacob, who at first decomposed ordinary acid by heating, but at a later date employed the gases generated by burning sulphur. In 1880 the price of fuming acid supplied from Kreuznach to the Höchst works was about 0·31 mark per kilo. It contained about 43 per cent. of free trioxide. Jacob sold his process shortly after to the Höchst works of Meister, Lucius, and Brüning. This firm has made fuming acid on a considerable scale ever since that time.

About the same time the Thann Chemical Works in Alsace made a contract with Chapman, Messel & Co. of Silvertown, for the purchase of Squire and Messel's patent of 1875; but while the preliminary investigations in regard to the establishment of the process were still proceeding, the Thann works acquired from Squire, who had no longer any connection with the Silvertown firm, a very much improved process. After trial experiments in 1879, this was found to give very satisfactory results. Silician sulphur was burnt in the usual manner, and the gases were treated with water in a column apparatus under a pressure of 4 atmospheres. The sulphur dioxide was expelled by steam from the solution thus obtained, mixed with the theoretical quantity of air and passed over heated platinised asbestos. The trioxide formed was absorbed in towers by concentrated sulphuric acid, and fuming acid of 40 per cent. was thus obtained. The exit-gases, still containing dioxide, were passed back into the process. The daily make was 30 cwt. of trioxide, and the yield 90 per cent. of the theoretical. At the beginning of 1881 this process was in regular working order at Thann, and it was subsequently also introduced at Ludwigshafen.

Winkler's process was also introduced in the *Müldener* smelting works at Freiberg in 1876, but before the erection of a large plant was commenced, on the lines of the experiments which had been made in these works, the Imperial Mining Office received a report from Winkler claiming that "the undersigned has succeeded in achieving a result regarded as impossible according to former experiments, viz., the production of sulphuric anhydride from a mixture of sulphur dioxide and atmospheric air."[1] Production on these lines was therefore undertaken at Freiberg, and attained some success on a large scale about December 1879. There were thus many competitors to the firm of Starck, who manufactured fuming acid by the Nordhausen process. This firm accordingly entered into combination with the manufacturers at Mannheim, Kreuznach, Höchst, and Thann, and the price of fuming acid was maintained at a high figure, until the *Badische* Company came into the market with such large quantities that the combine dissolved.

[1] Document unpublished until communicated by Winkler himself to Lunge (see previous edition of this book).

The plants devised to obtain sulphur dioxide from sulphuric acid had naturally a very short life. It was proposed at one time to employ plumbago retorts. Some factories seem to have employed platinum vessels, as mentioned in Squire and Messel's patent, but the action of very hot sulphuric acid on platinum is of course by no means negligible, and has been shown to depend to some extent on the nitrous and arsenious content of the acid.[1] The apparatus employed by Majert at Schlebusch, near Cologne, consisted of upright retorts made of a mixture of three parts of burnt fireclay and one part of Belgian clay, glazed with a mass which, at the highest temperature of the process, was pasty enough to fill up any cracks (see also Fr. P. 122130 of 1878). The retorts were perpendicular, entirely surrounded by the fire, and closed at top and bottom by "hydraulic" joints filled with molten glass. The acid flowed into the first retort through a platinum tube, so as not to touch the sides of the retort. It was evaporated within an inner cylinder, partly decomposed there and in the annular space between the cylinder and the retort, and completely in the second retort. The gases were conveyed from the first to the second retort by a twice-bent tube, which passed through the bottoms of both retorts, with a horizontal part which was surrounded by the flame of the fireplace. The gases passed away from the top of the second retort into a condenser for liquefying most of the water, then into a drying-tower, and at last into the catalytic apparatus for uniting sulphur dioxide and oxygen, consisting of cast-iron retorts filled with wire-gauze shelves, upon which the platinised asbestos was spread. According to Squire's patent of 1878 (Ger. P. 4285), strong sulphuric acid is introduced into a red-hot tower packed with hollow bricks.

The difficulties of such processes as these can be readily imagined, and after a few years the decomposition of sulphuric acid as a source of sulphur dioxide was generally abandoned owing to the extremely rapid disintegration of the plant. This tendency was manifest in the experiments made on many sides to utilise pyrites, or failing this, sulphur.

Nevertheless, the idea that the gases should be brought to the catalytic reaction in quantities represented by the

[1] Wagner's *Jahresber.*, 1877, 238.

equation of their combination still held ground, and for many years efforts were directed to finding more economical means of producing a gas mixture of this composition. Schröder and Hänisch, for instance, in 1887, proposed to replace the oxygen by air, and in order to compensate for the diluting effect of the nitrogen worked at a higher pressure than atmospheric "in order to bring the gas molecules closer together." Their patent (B. P. 9188 of 1887) states that a mixture of 25 per cent. of dioxide and 75 per cent. of air is to be made by means of a pump which automatically delivers the gases in the required volumes and compresses them to 2 to 3 atmospheres. This process appears to have had a certain practical vogue. Messel (B. P. 186 of 1878) recommended burning sulphur in pure oxygen obtained by electrolysis of water.

The third period of the historical development was thus concerned almost entirely with the application of Winkler's ideas. The decomposition of sulphuric acid was rapidly given up, but the idea persisted that excess of oxygen or any amount of nitrogen was fatal to success. Other peculiarities mark the efforts of this period. In every case the catalytic apparatus was externally heated; the thermal quality of the reaction had not been realised, and no stress seems to have been laid on temperature as a factor in conversion. Since no accurate pyrometers were available this is perhaps not surprising, and the discovery that for successful combination the heat of reaction must actually be *removed* lay far from the minds of inventors. Purification was little thought of; attempts to use the gases from ore-burning kilns were being made but were still in their infancy, and the experience required for the realisation of the facts concerned in this and other problems of the process was only to be gathered through the long series of experiments which were begun in all the large German works as soon as the manufacture of fuming acid by such processes began. None of the results were revealed until Knietsch, in his epoch-making lecture to the German Chemical Society in 1901, removed part of the veil which had concealed the long and careful plant-investigations of the *Badische* Company for many years. With Knietsch's lecture the fourth and last period may be said to have begun, and full success to have been attained.

An excellent instance of the uncertainty which surrounded the conclusions drawn from experiments in this third period is to be found in the relation of the experience of those responsible for carrying out the process in the *Müldener* smelting works at Freiberg. It has already been mentioned that these works, at Winkler's instigation, began the manufacture of fuming acid from pyrites burner-gases in 1879. During the first ten years of working the degree of combination was imperfect. The dioxide percentage of the kiln gases—originally 7 to 7·5 per cent.—was diminished only to about 4 per cent. by the catalyst, corresponding to a conversion of 45 per cent. This did not, as a matter of fact, seriously affect the prospects of the process, as the gases were afterwards delivered to vitriol-chambers. But it was noticed that the gas containing 4 per cent. of dioxide, if returned to the catalyst, could be reduced in dioxide content to 0·2 per cent., so that in all 95 per cent. conversion was reached by these means. In 1889 it was noticed that 85 to 90 per cent. conversion could be secured by one passage through the catalyst if the percentage of oxygen materially exceeded that of the sulphur dioxide, and after that only gases containing 6 per cent. of dioxide were employed. It has been pointed out by Haber[1] that the temperature at which a 45 per cent. conversion would be obtained from a 7·5 per cent. gas, even allowing that the oxygen present was 3·75 per cent. —the minimum possible—must have been about 640°. We know now that a catalyst so hot as this is incapable of giving a satisfactory yield with any usual gas-mixture. Further, the increase in conversion which was observed when the poorer gases containing only 4 per cent. of dioxide were returned to the catalyst is quite inexplicable on the basis of the increased oxygen content, and must be referred to the diminution in the heat of reaction, which would allow of the catalyst being cooler and therefore capable of better conversion. Similarly, the substitution of 6 per cent for 7·5 per cent. gases—even allowing for a very considerable increase in oxygen content—is quite insufficient to raise conversion from 45 to 85 per cent., and the reason for this more probably lies in the cooling effect of the dilution, diluted gases abstracting more of the heat of the reaction from the catalytic mass.

[1] *Thermodynamics of Technical Gas-Reactions*, 1908, 199.

It is evident in many ways that even when the elementary principles of mass action began to be understood, the thermal effects which complicate the reaction were lost sight of.

In concluding this account of the advances made before the Contact Process became really fruitful, it is interesting to note the part played by Clemens Winkler was a varied one. His arguments of 1873—that the gases should be present in molecular proportions—continued for twenty years or more to be accepted by all but a few who had found out that they were wrong. Among these was Winkler himself. In 1879 he had allied himself with the Freiberg works in the experiments on pyrites burner-gas. The *Rhenania* works at Stolberg followed the same lines, and in co-operation with him attained results which his first pronouncement stated to be impossible. Nothing more, however, was heard of Winkler. His recantation would, in all probability, have stimulated the growing industry even more than his earlier theories had undoubtedly done. No one discovered that Winkler himself had been the first to abandon these theories until 1900, when, in a lecture delivered in Hanover, he gave some account of the work carried out at Freiberg at his instigation.[1]

In 1901 Knietsch delivered his famous lecture before the German Chemical Society,[2] and described some of the work which had been carried out in the laboratories and in the plant of the *Badische* Company. This paper, in spite of defects and notwithstanding its many omissions, is still the most important ever written on the scientific and technical aspects of the oxidation of sulphur dioxide. Not only had Knietsch and his collaborators examined the behaviour of platinum and other catalysts under various conditions of temperature and rate of flow of the gas, and supplied much needed information about the physical properties of fuming acid and sulphur trioxide, and their action on iron and steel; they had also found solutions of all the technical problems which had made difficult the use of pyrites burner-gases, abandoned the theory of Winkler, arrived at the unexpected conclusion that contact vessels require cooling and not heating, and had, in general, rendered the contact process so successful that it could henceforward not only

[1] *Z. angew. Chem.*, 1900, 738.
[2] *Ber.*, 1901, 34, 4069-4115.

produce fuming acid cheaply, but actually compete with the chamber process for the manufacture of ordinary concentrated sulphuric acid.

The *Badische* Company originally procured its fuming acid from the firm of Starck, as did all other colour factories. The decomposition process of 1875 was investigated but found to be unsatisfactory, and experiments with burner gases from pyrites kilns were begun in 1881. For a time the process of Schröder and Hänisch—which has already been noted—was tried, but the experiments with burner gas were continued without interruption.

The first employment of burner gases gave very unsatisfactory results, and there seemed at first but little hope of success along this line. After a time the contact-mass lost its activity, even though the gases had been passed through various stages of purification—cooled in long pipes, washed with acid, and filtered through coke and asbestos. Further experiment revealed that minute amounts of certain substances deleterious to the contact-mass were carried through to the contact chambers by the sulphuric acid fog, which is always formed when sulphureous matter is burnt in moist air. Arsenic was found to be the most harmful of these impurities. In this way the fact was established that the problem of gas-purification was the most difficult of the problems which had to be solved. To this day gas-purification is the stage of the process which falls furthest from perfection, gives most trouble, and is the weakest point of many well-known types of contact plant.

Nevertheless, to use the words of Knietsch, the investigators of the *Badische* had succeeded in charting accurately the rocks on which so many of their forerunners had been wrecked. Experiment after experiment was made, at an enormous cost of time, labour, and patience, and even after the introduction of the complete process on a large scale, some years passed before the freedom of the gases from impurities could be assured. The final result (Ger. P. 113933 of 1898) was that every perceptible trace of impurity could be removed if, as the last stage of the purification, the gases were submitted to continuous and systematic washing with water or dilute acid. Even after this other irregularities appeared, and the origin of each had laboriously to be found and a method devised for removing it.

The other results and data reported by Knietsch, both scientific and technical, will be referred to in the sequel as opportunity arises.

The annual production of sulphuric anhydride at the Ludwigshafen works of the *Badische*, during the years when these important investigations were in progress, has been given by Knietsch: In 1888, 18,500 tons; 1894, 39,000 tons; 1899, 89,600 tons; and in 1900, 116,000 tons. At the present time the needs of the German dye manufacture are supplied entirely by contact plants, the chambers which formerly existed having been pulled down.

The patents of the *Verein Chemischer Fabriken in Mannheim* were taken out in 1898 and 1899. The Mannheim process introduced a new principle into the manufacture, viz.: The conversion of sulphur dioxide in two stages, first by ferric oxide and then by platinum in another contact space. Purification of the gases before coming into contact with the platinum was effected by filtration through porous, granular, or fibrous substances. A special form of kiln for burning the pyrites was devised so that the air used for combustion could be dried before use. The conditions under which ferric oxide functions as a catalyst were found by many observers to be quite different from those holding in the case of platinum, and this catalyst possesses a literature almost entirely its own.

The years 1898 to 1902 were indeed the most prolific in the history of this branch of acid manufacture. The patents taken out by Schröder and Grillo (*Aktiengesellschaft für Zinkindustrie vormals W. Grillo*) date also from this period. The Schröder-Grillo process was originally devised to find an outlet for the supplies of liquid sulphur dioxide (produced from the roasting of zinc ores), which the Grillo firm found difficult to sell. The guiding idea was that the previous ill success of similar processes had been due to defective contact between the gases and the catalyst. Such a defect, if it existed, would be likely to occur in an accentuated form when such rich gases were used as the Grillo firm wished to employ. The reaction space was therefore filled as completely as possible and the contact-mass was very tightly packed. On a bottom of fine stone material a dense plug of platinised asbestos (8 to 10 per cent. platinum) was placed and firmly compressed by means of a

metal disc. In order to prevent the formation of continuous channels another layer of stone was put in, and again a firm asbestos plug about ½ in. thick. Fifteen such layers were placed in each pipe. The resistance of these converters was very high, and the gas mixture, consisting of 25 per cent. of dioxide and 75 per cent. of air, was forced through by a cylindrical air compressor (B. P. 9188 of 1887). The degree of conversion was said to be relatively high, about 95 per cent.

This process was worked out on an experimental plant at Hamborn, and in 1887 was transferred to the *Badische* Company, who worked it for some years with inconclusive results. The *Badische*, however, had found, in their experiments with pyrites burner-gases, more profitable fields, and the Grillo process in its original form was therefore abandoned. In 1897 the agreement between the two firms came to an end, and the Hamborn experiments were recommenced, in order to deal with the roasting gases from the blende furnaces. For these diluted gases a less resistant contact-mass had to be found, and it was desired to apply the platinum in such a way that the contact-mass could be regenerated after it had failed in activity on account of "poisoning." This eventuality is always to be feared in connection with blende roasting—a process from which several deleterious substances, including silicon-fluoride, are known to be evolved. These considerations led to the abandonment of the usual substrata for the platinum and the substitution of soluble metallic sulphates (B. P. 25158 of 1898). Magnesium sulphate was found to possess exceptional advantages in this connection, and is indeed, to-day, one of the best known bases of contact-mass. When regeneration is required the mass can, in the last resort, be dissolved in water, and the finely divided platinum recovered. In addition to various patents relative to the methods of mass-regeneration, the Grillo firm devised an improved form of converter (B. P. 17034 of 1900), in which, by means of perforated metallic diaphragms, the mass was distributed in several layers through which the gases passed successively. In this way the contact between gas and solid was improved, and the development of the heat of reaction made more even. The Grillo converter of the present day still conforms to the original idea of 1900.

In the beginning of 1902 ten factories were working the

Grillo process—four of these being in Germany—and twelve more factories were in course of erection. This process has been very generally adopted in many countries. The Grillo converter, and certain other sections of the plant have received sustained elaboration in the United States. Grillo plants of very large capacity (in addition to Mannheim units erected as a temporary measure to secure almost immediate production) were erected on several sites in this country during the War, by the Department of Explosives Supply.

The Tentelew process came to maturity a few years later than those which have already been mentioned. The patents covering the various stages of the process were taken out in the names of Eschellman, Harmuth, and the Tentelew Chemical Company of St Petersburg, in the years 1902 to 1909. Until 1886 all the fuming sulphuric acid consumed in the manufacture of lubricating oils from Russian crude naphtha had been obtained from the firm of Starck, but in that year the Tentelew Company began the experiments which, in 1896, resulted in a process which was distinguished by a thorough purification of the burner-gas and by the operation of a converter having the contact-mass arranged in several sections. In 1901 patents were applied for in nearly all countries. The applications were contested by the *Badische* but the opposition failed.

The Tentelew patents did not add much which was in principle new, but the process had been carefully worked out along lines similar to these which already had led to success in other countries. It is now a very highly developed and successful method of manufacture, and plants are working in many parts of the world. At the end of 1911, twenty-four sets of plant were said to be in operation.

In Britain, prior to the War, the Contact Process had reached no great production. The Silvertown works of Messrs Spencer, Chapman & Messel, at which much of the earlier experimental work was carried out, had continued to supply a large part of the oleum required for sale, and are in active operation at the present time. There were, in addition, one large Mannheim and one Tentelew installation, operated in succession by Messrs Nobels, besides several smaller Mannheims, either of the complete design, or operating ferric oxide contacts in connection with chambers. The production was quite insufficient for war

purposes, and was augmented by the construction of many plants of great size and various designs.

In the United States all three processes, Grillo, Mannheim, and Tentelew, have been used, and the first in particular has received very full development. The important German patents were acquired at an early date by the General Chemical Company of New York, which now owns or controls all the patents of these three processes, and many others in addition. The New Jersey Zinc Company was the owner of the Grillo-Schröder patents, but after litigation these also passed to the company first mentioned, which issues a licence and requires royalties for the installation and operation of all contact plants.[1]

The first successful introduction of the Contact Process into the United States is said to have been in 1898, when the *Badische* erected an experimental plant in New Jersey. A few years later, in 1899, the Mineral Point Zinc Company erected a Grillo plant to utilise the gas from blende-roasting; but the necessary details were not well worked out and the enterprise was a failure. The first plant on the Herreshof system was erected by the General Chemical Company in 1900, and the contact-mass was in use for ten years without renewal. This was the first contact plant in the States to burn arsenical pyrites.[2] There are now in all forty-eight plants of which the General Chemical Company own nine.[3] In the hands of this firm the Contact Process has attained what is probably its most modern development. One of the principal points is the employment of duplicate heat-exchangers and converters, with the effect of facilitating the regeneration of the heat of reaction, and of reducing greatly the necessary amount of platinum. They have also introduced what appear to be very considerable changes into the purification system, and the new plant at Dormagen which embodies all these developments, and also the addition of Cottrell dust precipitators, is said to have been built from their designs.

In France the normal production of oleum was very low as there were only a few very small plants at Saint Gobain and

[1] *U.S. Bureau of Mines, Bull.* 1920, 184, 152.
[2] Lunge, *Z. angew. Chem.*, 1910, 24, 721.
[3] *U.S. Bureau of Mines, Bull.* 1920, 184, 13.

elsewhere. During the War a number of pyrites-burning Grillo plants were erected by the Paris house of the Simon-Carvés Company.

With this summary of the history of the more known types of plant, the historical survey of the process may fitly be brought to a close. Further details are to be found attached to the descriptions which are given later of individual plants and their operation. Sufficient has already been said to indicate the extent to which the discovery made by Peregrine Phillips nearly a hundred years ago, has been expanded, and to demonstrate, in this case as in many others, that achievements of vast importance may have their origin in very uncertain and tentative efforts.

The Nordhausen and Similar Processes.

Although this treatise deals only with the manufacture of fuming sulphuric acid by Contact Processes—no other process now being used—the manufacture by some other methods possesses a certain historical interest and will be described briefly.

It is probable that the fuming variety of sulphuric acid was the earliest which was produced for sale. Its manufacture in Bohemia was of very early origin. During the Thirty Years' War the industry was destroyed in Bohemia and was transferred to the Harz country. Factories were located at Braunlage and Goslar, and the acid was stored in a warehouse at Nordhausen, from which this commodity took the name by which it was long known. In 1778 the industry was re-established in Bohemia, at first on a small scale, but later, in 1792, the scale of the operations was increased by Johann David Starck, who carried out the process with the assistance of workmen from the Nordhausen factories.

The raw material consisted of certain slates which contained a considerable amount of pyrites. The presence of iron, and alumina in these slates had led to their use, since the sixteenth century, for the production of alum, or of copperas and ferric sulphate (*vitriolstein*). It is easy to see how the availability of ferric sulphate led to the manufacture of fuming acid.

The manufacture was carried out in the following way:[1]

[1] Wagner's *Jahresber.*, 1873, 220.

The slate, after being broken up, was piled in terrace-shaped heaps, space being left for air to circulate through horizontal and vertical channels. Arrangements were made for spraying water over all the heaps. The pyrites in the slate was oxidised during the weathering, so that the liquor obtained by lixiviation contained ferric sulphate, and a little aluminium sulphate. These liquors were evaporated to dryness, at first by spontaneous evaporation in the air, then by boiling-down over a fire in brick furnaces, and finally by boiling in cast-iron boilers. The product was run from the boilers and allowed to solidify. The mass was of a greenish colour and consisted mainly of

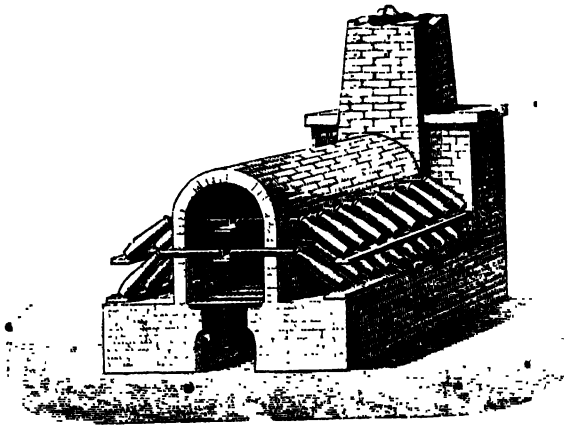


FIG. 1.

ferric sulphate and variable amounts of ferrous, aluminium, and magnesium sulphates. From 6 to 20 tons of slate were required to make 1 ton of "vitriol-stone." The yield of "oleum" (*oleum vitrioli*) was at first 33 per cent.; later on it was 40 to 50 per cent.

The "vitriol-stone" was calcined in four works containing 120 galley furnaces, which were similar to that shown in Fig. 1, except that they contained five tiers of retorts instead of two. Each furnace contained 306 retorts, to each of which was fitted a receiver large enough to contain the product of four or five distillations. In every retort was placed a charge of about three-quarters of a kilo of the crude "stone." The neck of each retort fitted into its receiver, and the joint was made tight with

clay in such a way that the luting material could not fall into the acid. The consumption of retorts at Starck's works was 224,000 per annum, in addition to 40,000 receivers.

From the beginning of the distillation the temperature was slowly raised, so that after four hours the bottom tier of retorts had only just attained a red heat. During this time the retorts were not closed to the atmosphere, and the remaining ferrous sulphate was in great part oxidised. As the temperature rose, water vapour and sulphur dioxide began to issue from the necks and were followed soon after by thick fumes of sulphuric anhydride. The receivers were then fitted, each receiver having been previously partly filled with either a quarter of a kilo of water, or with a corresponding quantity of sulphuric acid. The distillation was repeated again and again until the liquid in the receivers had risen sufficiently in gravity. When acid of 66° Bé. (1·84) had been used as condensing liquid, three or four distillations were required to attain the desired concentration of about 65 per cent. of pure trioxide. The workmen recognised that a sufficient strength had been reached by dipping a wooden splinter into the acid, and noting the speed of charring. The acid was stored in bulk and drawn off when required from the impurities which had settled to the bottom.

The ferric oxide remaining in the retorts was known as *caput mortuum*, *colcothar*, or *English Red*, and in Britain as *Venetian Red*. It was sold, after special treatment carried out to improve the shade and ensure the necessary fineness, as a pigment. This branch of the manufacture was very much improved by Starck, so that in 1872 1000 tons were sold in nineteen shades and forty-one grades. It was ground under mill-stones and calcined with various proportions of common salt. Yellow shades were obtained by igniting for an hour with 2 per cent. of salt, brown shades by adding 4 per cent. of salt, purple shades by igniting for six hours at an increasing temperature with 6 per cent. of salt, and so on.

It is stated that even under the most favourable circumstances 100 parts of ferric sulphate containing 52 to 54 parts of anhydride, did not yield more than 36 on distillation. In 1792 1 cwt. of fuming oil of vitriol cost in Bohemia about £5; in 1873 about £1. In 1832 about 1000 tons were produced; in 1846 about 3000; in 1873, 3360; and in 1884, 4350 tons.

It has already been seen that after 1875 the monopoly of the Starck firm began to be menaced seriously by various contact processes. In 1894 the last galley furnace was closed down at Bras, and in 1900 the whole Bohemian manufacture carried out on these lines, came to an end.

The yield from the "Nordhausen" process could never be a satisfactory one, for the temperature of dissociation of ferric sulphate into oxide of iron and sulphuric anhydride is fairly high (although lower than the corresponding temperatures for the other common metallic sulphates), so that the anhydride when formed was liable to considerable decomposition into sulphur dioxide and oxygen—a change which was favoured by the presence of the catalysing ferric oxide produced by the reaction. The possibility of obtaining sulphuric anhydride by means of ferric sulphate, *indirectly*, will be discussed later. It may be noted in passing that, according to the work of Keppeler and D'Ans,[1] the dissociation pressure of anhydride from ferric sulphate at 640° C. is only 15 mm. The temperature reached must, therefore, have been far higher than this, and the amount of decomposition must have been great. It was stated, for instance, by Schuberth (Ger. P. 52000 of 1889), that in the best cases loss from decomposition into dioxide and oxygen amounted to 30 per cent. of the total possible anhydride and that, if large retorts were used, no anhydride might be produced at all. For this reason the process had always been carried out with very small vessels by means of a necessarily large amount of skilled labour.

Many proposals were made to improve the process. Schubert, for instance (*loc. cit.*), in what was practically a scheme for the addition of a contact process, proposed to conduct the distillation under a vacuum and to pass the gases drawn away from the retorts, after the removal of the anhydride, over a contact mass containing platinum. The residue in the retorts was to be mixed with oil of vitriol and distilled again. This suggestion illustrates a tendency which was very manifest at the time—to endeavour to utilise ferric sulphate made artificially from its component oxide and acid, and thus to evade the natural monopoly of the firm of Starck.

Processes employing other Sulphates.—Many attempts

[1] *Z. physik. Chem.*, 1908, 62, 89.

have been made since the early days of chemistry to prepare acid containing pure trioxide from sodium bisulphate, with more or less success. In a patent taken out by Prelier in 1847, it was proposed to heat sodium, potassium, or calcium sulphate with a sufficient quantity of acid to form bisulphate. First of all water distilled over, then sulphuric acid of increasing strength, and finally fuming acid. After the distillation the residue in the retort could be used again. In another patent (Wallace, B. P. 2285 of 1876) sodium bisulphate was to be heated in fireclay retorts. The fumes coming over first of all were to be condensed separately, and the final distillate condensed directly in the jars in which it was to be transported. By adding more acid the residue in the retort could be used over again, as in the previous proposal.

It is believed that the bisulphate process was actually in operation at the works of G. C. Zimmer, in Mannheim, in 1877, and for a number of years after, and that 40 per cent. oleum made by it was delivered to the *Badische* works.[1] More recent patents in connection with the production of pyrosulphates, and information bearing on the chemistry of this method of producing oleum will be found in Chapter II.

The addition of magnesium sulphate to the sodium salt was said to be an advantage. In a patent taken out by Wolters (Ger. P. 3110 of 1878), it is stated that the liberation of sulphur trioxide from sodium or potassium pyrosulphate takes place at a lower temperature if magnesium sulphate is added, so that the dissociation is less, and the erosion of the containing vessels not so great. On the large scale this process does not seem to have been successful. Another device for lowering the temperature of decomposition of the pyrosulphate, due to the same worker (Ger. P. 12295 of 1881), was to heat the bisulphate as usual until the water had been expelled, and then to add sulphuric acid, free from water, to the residue. A decomposition resulted in the sense of the equation—

$$Na_2S_2O_7 + H_2SO_4 = 2NaHSO_4 + SO_3$$

and the trioxide could readily be distilled away, the bisulphate being treated over again. This process was actually worked at Einergraben near Barmen, and at several other factories during the years 1884 to 1889.

[1] Lunge, Fourth Edition of this work.

CHAPTER II

THE PROPERTIES AND ANALYSIS OF SULPHUR TRIOXIDE AND OLEUM

SULPHUR TRIOXIDE, SO_3 (*Molecular Weight* = 80·06).

SULPHUR trioxide is said to have been described by Basil Valentine towards the end of the fifteenth century under the name of "philosophical salt." It was obtained by the distillation of fuming sulphuric acid by Lennerz in 1675. Scheele and Guyton de Morveau both recognised, about 1786, that the substance was the anhydride of sulphuric acid.

Formation.—In addition to the catalytic addition of oxygen to sulphur dioxide, which will not be noticed further here, the trioxide arises under a variety of conditions.

(i) By the decomposition of sulphur dioxide under the action of light. If an intense beam of light be passed through it, as in Tyndall's experiments, the gas becomes cloudy, owing to the formation of trioxide.[1]

(ii) By the action of electric sparks. If a spark discharge is passed through the dioxide a slow decomposition into trioxide and sulphur ensues but does not proceed to completion, for the reaction is a balanced one. The decomposition becomes complete if water or sulphuric acid is present to absorb the trioxide.[2]

(iii) Passed through a mixture of two volumes of dioxide with one of oxygen, the spark discharge leads to the same result—an equilibrium being set up.[3] According to Berthelot, the compound S_2O_7 is formed in this way if certain conditions are secured.[4] It may be noted that the silent electric discharge

[1] Morren, *Comptes rend.*, 1869, **69**, 397.

[2] Buff and Hofmann, *Annalen*, 1860, **113**, 129; Deville, *Bull. Soc. chim.*, 1865; [II], **3**, 366; Berthelot, *Comptes rend.*, 1883, **96**, 298.

[3] Buff and Hofmann, *loc. cit.* [4] Berthelot, *Comptes rend.*, 1878, **86**, 20.

also causes the oxidation of the dioxide, but that persulphuric anhydride results, and not the trioxide.[1]

(iv) Ozone readily oxidises the dioxide at atmospheric temperature, giving sulphuric acid or anhydride in the presence or absence, respectively, of water vapour.[2] Several patents for acid manufacture have been taken out on these lines.

(v) The combustion of sulphur in air or oxygen gives rise to a certain amount of trioxide. Hempel found that in oxygen at atmospheric pressure the sulphur converted to trioxide was about 2 per cent. of the total amount burnt. Increase of pressure raised the proportion, and in oxygen at 50 atmospheres pressure, it was 50 per cent.[3] A more recent investigation showed that in air the percentage may be as high as 7. Moisture has no effect on the reaction, and the higher yield is ascribed to the catalytic activity of nitrogen compounds which are probably present.[4] Norrish and Rideal investigated the reaction between sulphur and oxygen by a dynamic flow method between 235° and 385°. They found that the formation of trioxide became appreciable at 305°, and increased rapidly above this temperature.[5] An explanation of these facts may not be evident, but the facts themselves are significant in connection with the large-scale combustion of sulphur.

(vi) About the same proportion (6 to 8 per cent.) of the combined sulphur in illuminating gas is converted into trioxide when the gas is burnt.[6]

(vii) At very high temperatures (*e.g.* about 1200°) sulphur dioxide is partially resolved into sulphur and trioxide.[7] At this temperature the proportion of trioxide capable of existence is small in any case.

Preparation.—Small quantities of sulphur trioxide are best prepared by distilling oleum, and condensing the vapour of the trioxide in an ice-cooled receiver. The distillate usually contains some dioxide as well as other impurities and, if pure

[1] Berthelot, *loc. cit.* [2] Borchers, Das Ozon, Fonrobert, Stuttgart, 1916.
[3] *Ber.*, 1890, **22**, 1455.
[4] Kastle and M'Hargue, *Amer. Chem. J.*, 1907, **38**, 465.
[5] *J. Chem. Soc. Trans*, 1923, **128**, 3202.
[6] Dennstedt and Ahrens, *Z. anal. Chem.*, 1896, **35**, 1.
[7] Walden and Centnerszwer, *Z. physik. Chem.*, 1902, **42**, 432.

material is required, must be redistilled once or several times. Phosphorus pentoxide may be added before distillation. Very pure specimens were prepared by Lichty,[1] who distilled them repeatedly from phosphorus pentoxide in specially evacuated apparatus.[2] An investigation of the purified substance has also been made recently by Berthoud.[3]

Properties.—Sulphur trioxide exists in two modifications, the relation of which is not yet definitely known. The first or α-modification boils about 17° and melts about 45°. The other (or β variety) has no melting-point under atmospheric pressure. The isomeric relation of these two bodies was maintained by Marignac and others in 1853 and onwards, but was denied by Weber in 1876, who believed that the difference was due to hydration of the second variety, and by Rabs in 1888.[4] Oddo claimed to have confirmed the isomerism. Lichty[5] produced evidence pointing in the same direction, but doubt is thrown on it by Berthoud,[6] and the exact nature of the relation cannot yet be considered to be decided.

The α-Trioxide.—The crystals formed by the solidification of the freshly prepared liquid are long, transparent, rod-like needles. The liquid substance is nearly as fluid as water. The melting-point is 16·88° (Lichty, 16·35°—Berthoud). The substance is susceptible of considerable supercooling. The boiling-point is 44·88° (Lichty, 44·52°—Berthoud) at 760·0 mm. The coefficient of expansion is very large, as can be seen from the following values of the density (Lichty):—

$t°$ =	11·8	15	20	25	30	35	40	48
D =	1·9457	1·9422	1·9229	1·9020	1·8798	1·8569	1·8324	1·7931

Berthoud made a series of measurements of the vapour tension, from which the following are selected:—[7]

$t°$	24	25	33·4	36·6	29·8	42·2	45·4	47·8
p (mm. mercury)	240·5	253·5	421·0	500·0	592	678	793·8	887·2
$t°$	98·2	134·5	159·1	179·9	192·6	205·4	216·9	218·2 (c)
pa (atmospheres)	9·2	18·7	30·4	43·9	55·2	66·9	80·4	83·8 (c)

[1] *J. Amer. Chem. Soc.*, 1912, **34**, 1440. [2] *J. Amer. Chem. Soc.*, **30**, 1835. [3] *Helv. Chim. Acta*, 1922, **5**, 513.

[4] For references see *Gmelin Kraut*, 1 [I], 474. [5] *loc. cit.* [6] *loc. cit.*

[7] Up to 48°, p is represented by the equation—

$$\log_{10} p = -\frac{2324}{T} + 10{\cdot}17.$$

The last figures given are the critical temperature and pressure. For the critical temperature, Schenk[1] found 216°. The vapour density corresponds to the simple formula SO_3.[2] Some further information will be found in the account of the properties of oleum. The specific heat between 25° and 35° was found by Knietsch to be 0·77. Sulphur trioxide is a non-conductor of electricity, and according to Walden has no ionising power as a solvent. Trouton's constant has the high value of 32·5, and the liquid is highly associated. Between 29·5° and 78° it is said to be represented by the formula S_2O_6.[3]

Thermal Data.—The thermal constants relating to this substance and to its formation are very sparse and uncertain. The determinations of the heat of formation by Berthelot[4] and Thomsen[5] were of course not obtained by direct measurement, but by calorimetric investigation of changes which occur at the ordinary pressure and temperature—such as the oxidation of aqueous sulphurous acid by chlorine. Much of the uncertainty originates in the fact that there is a marked discrepancy between the two very carefully executed series of determinations by these two workers of the heat of formation of sulphur dioxide from orthorhombic sulphur. The available results are given below in kilocalories per gram-molecule of dioxide:—

	Berthelot.	Thomsen.
(1) $S + O_2 \longrightarrow SO_2$ (gas)	69·3	71·1
(2) $S + O_3 \longrightarrow SO_3$ (gas)	91·9	...
(3) „ „ (liquid) . . .	...	103·24
(4) „ „ (solid) . . .	103·7	...
(5) „ „ (dissolved) . . .	141·0	142·41

By ("dissolved") is meant that water was present in very great excess. Berthelot's figures gives 22·6 for the formation of gaseous trioxide, but we cannot deduce a corresponding value from Thomsen's results, since the latent heat of vaporisation of the trioxide has not been directly determined. We can, however, employ the value deduced by Porter[6] from Knietsch's vapour pressure measurements—9·6 at 20°—and so obtain from

[1] *Annalen*, 1901, **316**, 1.
[2] Perman, *Proc. Roy. Soc.*, 1899, **48**, 57.
[3] Berthoud, *Ann. Chim. Phys.*, 1923, **20**, 77.
[4] *Thermochemie*, **2**, 91.
[5] *Chem. Untersuchungen*, **2**, 254.
[6] *Trans. Faraday Soc.*, 1917, **13**, 373.

this and (1) and (3) above the figure 22·5[1] kilocalories. The two values agree well in spite of some doubt about both. The value 22·6 is taken throughout this book, in reference to constant pressure.

The heat of vaporisation of *solid* trioxide was given as 11·8 kilocalories by Berthelot.[2] This is the value involved in the left-hand column of figures in the table above. The corresponding quantity for the liquid substance is given by Porter[3] as 9·00 at 90°, 9·36 at 40°, 9·60 at 20°, and 9·71 at 0°. For the range 23° to 44° Berthoud deduces the value 10·30 from his measurements of the vapour tension of the trioxide. Subtracting Porter's value at 18° from Berthelot's figure, we obtain 2·20 as the latent heat of fusion. For this Porter deduces the value 1·84 from Knietsch's figures for the heat of solution of liquid and solid oleum (*q.v.*).

For the reaction—SO_3 (liquid) + H_2O (liquid) $\rightarrow$ H_2SO_4 (liquid)—Thomsen found a development of 21·3 kilocalories. Further data will be found under "Oleum."

There is need for more precise knowledge of these thermal constants.

The β Trioxide.—If the liquid trioxide is preserved for some time at about 25°, or is frequently melted and remelted, bunches of fine needles form and grow, so that finally the whole liquid is converted into a white felted silky mass of the β modification. This does not melt under ordinary pressure, but gradually passes into vapour when heated to 50° or over. The β modification forms fine, feathery, asbestos-like crystals which are tough and in the massive state difficult to divide. Its density at 20° is 1·97.[4] In an evacuated tube it vaporises slowly, although it shows at first no considerable vapour pressure.

The transition of the α to the β form is assisted by traces of water. Although the existence of the two modifications has been established, their relation to each other is not yet clear.

[1] It is not certainly known whether Berthelot's value, at least, applied to constant pressure or constant volume, but the possible difference from this cause, about 0·3 kilocalorie, is insignificant in view of the much greater uncertainty affecting both values. See also Bodenstein and Pohl's values at high temperatures, given in Chapter III.

[2] *Comptes rend.*, 1880, 90, 1510.

[3] *loc. cit.*

[4] Oddo, *Gaz. chim.*, 1901, 31, II, 158.

both modifications have the same vapour density. Oddo, by cryoscopic determination in phosphorus oxychloride, claimed to have proved that the β variety was S_2O_6, *i.e.*, was the dimeric modification of the other. The later work by Lichty assigns the simple formula to both modifications in solution. Oddo claimed that the transition from the α to the β form was possible in the entire absence of water, but doubt has been thrown on the truth of this by the more recent work carried out by Berthoud.[1] This investigator prepared the pure α modification by repeated distillation *in vacuo*, and preserved the distillate in sealed tubes. The transition to the β form always began at once and extended over several days but was in no case complete. Tubes which each contained a mixture of the α and β form, the former being liquid or solid in accordance with the atmospheric temperature, were preserved for four years, and throughout this time the proportion of the two substances remained unchanged. This fact may be held to render unsound the generally accepted hypothesis that the β modification is simply an isomer of the other, for it is difficult to explain in that way the termination of the change before it is complete. Attention is therefore redirected to the idea of Weber, according to which the water inevitably present is the essential agent in the transition. The β form is a "product of hydration," and when the water available has been used up, no further transition can occur. It is believed that the water cannot exceed one part in a million of the whole substance.

If this much discussed substance were a simple isomer it might be expected to have definite and invariable properties, but according to Berthoud such properties cannot be assigned to it. Commercial trioxide (consisting mainly or entirely of β) was heated in a sealed flask. Fusion began at 55° and was not complete after this temperature had been maintained for twenty-four hours. At 68° a new condition of equilibrium between solid and liquid was set up, and the whole was melted only by heating to 80° or 90°. The melting-point of the sublimed substance was 35° or higher, and was thought to vary with the hydration in a continuous way. Nor can the substance be distilled (under pressure) at a constant temperature. As the distillation proceeded the temperature was necessarily raised

[1] *Helv. Chim. Acta*, 1922, 5, 513.

more and more. The isomerism of sulphur trioxide seems to be apparent in the solid state only. It is initiated by, and probably dependent on, the presence of minute amounts of water.

The mystery in which the polymerism of this substance is involved has been increased by the most recent work carried out by Le Blanc and Rühle.[1] The trioxide was synthesised photochemically at a temperature of 150° and at pressures of a few tenths of an atmosphere, and condensed on formation, even at these low pressures, to a solid. The vapour pressure of this solid, however, had no constant value. It was found also that the solid trioxide melted about 17°, but on repeated melting the fraction remaining unmelted above this temperature increased. Distillation at low pressures was then investigated, and in this way, it is claimed, no less than four modifications of the substance (admittedly not very sharply defined) were observed. The first modification (*a*) melted at 95-100°, had a vapour pressure of about 17·5 mm. at 0°, and condensed throughout the apparatus in needles; the second (*b*) was formed as a dull, porcelain-like mass by condensation at 0°, melted about 31°, and had a vapour-pressure of 25-30 mm. at 0°; the third and fourth varieties (*c* and *d*) both melted at 16·8°, but differed in appearance and behaviour on cooling. It was found that (*c*) readily passed into (*a*) and (*b*). The vapour pressure of (*c*) at 0° was at least 195 mm.; that of (*d*) was undeterminable.

Chemical Reaction.—The chemical behaviour of the two modifications is the same, but the *a* modification is the more active. In moist air sulphur trioxide at once forms dense white fumes, which are naturally very corrosive and poisonous. On immersion in water the substance hisses like red-hot iron, and if certain proportions are used (4 parts anhydride and 1 part water) the combined mass is completely vaporised, light being emitted. The anhydride has an intense dehydrating action—the β less than the *a* variety. It has been stated that the β substance can be touched with the dry fingers without the skin being seriously damaged. The *a* variety on the other hand chars the skin, or any other organic matter, at once. A note should be made that in spite of the great affinity of this substance for water, it is impossible to retain more

[1] *Chem. Zentr.*, 1923, 94 [iv.], 522.

than a small proportion of it by absorption of the vapour in water. This subject will be discussed more fully later.

None of the metals Zn, Sn, Pb, Fe, Cu, Hg, Na is attacked by the dry vapour, and no reaction takes place with many basic oxides such as lime and copper oxide,[1] if these are carefully dried. The anhydride manifests a powerful oxidising action under ordinary conditions. Phosphorus inflames in the vapour, liberating sulphur. Phosphorous acid is converted into the compound $H_3PO_4,2SO_2$. Phosphorus and the liquid anhydride yield the compound $3P_2O_4,2SO_3$. Phosphorus trichloride is oxidised to oxychloride, hydrobromic and hydriodic acids to their respective halogens.

With sulphur the blue compound S_2O_3 is formed; with selenium the green $SeSO_3$; with tellurium the red $TeSO_3$. By absorbing sulphur dioxide in the cooled trioxide a liquid is formed which appears to contain the compound $SO_2,2SO_3$.

The addition of nitric acid of high concentration to oleum has often been investigated in view of the lowering of the freezing-point which results, and the consequently reduced liability to freeze during transport. According to an American patent (Schultz and the General Chemical Co., U.S. P. 1047576), a compound of the composition $N_2O_5(SO_3)4,H_2O$ can be made in several technically convenient ways. For instance, a mixture of 300 parts of 60 per cent. oleum and 70 parts of nitric acid of 96 per cent. HNO_3 may be treated with the vapours of sulphur trioxide and nitric acid with suitable gentle heating. The substance obtained does not fume in air and is a crystalline and hygroscopic solid. The specific gravity is 2·18 and the melting-point lies between 93° and 104°. A higher temperature is required to effect decomposition—effervescence takes place at 170°. The material is easily packed for transport and is of very uniform composition.

Since the Contact Process came into active operation, sulphuric anhydride has become an easily obtainable commercial material and is employed in several manufactures, although its solution in sulphuric acid is, in general, more convenient and far more widely used. The trioxide is sent out in sealed drums of tinned iron. No precautions taken in handling this substance, or indeed oleum itself, can

[1] Baker, *J. Chem. Soc. Trans.*, 1894, 65, 611.

be considered excessive, for burns with the liquid trioxide, or with trioxide which is just beginning to liquefy with absorbed moisture, or burns with oleum, are instantaneous on contact. They frequently become septic and are always very slow to heal.

Chlorsulphonic Anhydride, SO_3HCl.

(*Molecular Weight* = 116·53.)

Chlorsulphonic anhydride is a substance of some commercial importance. It is obtained directly from oleum and has proved of use in warfare for the production of smoke clouds.

Formation.—(i) By the direct union of hydrochloric acid and sulphuric anhydride. (ii) By the action of phosphorus tri-, penta-, or oxy-chloride on concentrated sulphuric acid. (iii) From sulphuryl chloride, by the action of damp air—$SO_2Cl_2 + H_2O = SO_3HCl + HCl$, or from pyrosulphuryl chloride by reaction with water—$S_2O_5Cl_2 + H_2O = 2SO_3HCl$, and in several other ways. It is most conveniently prepared on a small scale either by passing hydrochloric acid into oleum and distilling the product, or by utilising the reaction of phosphorus pentachloride on concentrated sulphuric acid. In the second case the mixture divides into two layers when sufficient pentachloride has been added and is then distilled.

Properties and Reactions.—Chlorsulphonic anhydride is a colourless liquid. It has a penetrating and unpleasant odour and a very corrosive action on the skin. Its density at 0° is 1·78474, and at 155·3°—the boiling-point—is 1·54874.[1] When boiled it decomposes to some extent into its constituents. Many salts are dissolved by the anhydride. The specific electrical conductivity is given by Walden as $0·172 \times 10^{-3}$. The specific heat at 15° to 18° is 0·282, the latent heat of vaporisation for 1 gram-molecule is 12·8 kilogram calories, and the heat of the reaction SO_3 (solid) + HCl (gas) → SO_3HCl (fluid) is 14·4 kilocalories—directly determined calorimetrically by Ogier.

The substance reacts violently with water, decomposing into its constituent acids. Addition of concentrated sulphuric acid causes formation of oleum and hydrochloric acid. Sulphur and hydrogen sulphide are oxidised by it in complex reactions. By the action of phosphorus pentachloride pyrosulphuryl

[1] Thorpe, *J. Chem. Soc. Trans.*, 1880, 37, 358.

chloride is formed—$2SO_3HCl+PCl_5=S_2O_5Cl_2+POCl_3+HCl$. Sulphates of the alkalies and alkaline earths are converted into pyrosulphates, and sodium chloride forms the chlorosulphonate $NaO-SO_2Cl$.

Chlorsulphonic anhydride reacts with alcohols and with many other substances of the aliphatic series, but is chiefly useful as a sulphonating reagent for aromatic hydrocarbons. The *o*-toluene sulphonic acid required for the manufacture of saccharin is best made in this way and, as in many other similar cases, is obtained in the form of the acid chloride.

Manufacture.—On a large scale the anhydride is made by passing hydrochloric acid gas into concentrated oleum. At the Höchst works in 1919 the gas was produced by the interaction of nitre cake and salt in Mactear furnaces, this method being preferred to that using sulphuric acid and salt on account of the higher purity of the gas generated. The reaction was carried out in two cast-iron vessels worked in series. The first held—at the beginning of a cycle—a charge obtained by a previous operation in the second vessel, and the second vessel contained 60 per cent. oleum. Dried hydrochloric acid was passed into the first vessel through an earthen dip-pipe and thence to the second vessel by means of an iron pipe. The waste gas was removed to a water-fed scrubber by means of an earthenware air-ejector. The temperature in the first vessel rose rapidly during the absorption to 100° or 110° and remained fairly constant until the saturation was complete, and then fell.

The resulting solution of the anhydride in sulphuric acid was distilled from a cast-iron vessel through an iron column, the residual sulphuric acid being stated to contain no hydrochloric acid.

Pyrosulphuric Acid, $H_2S_2O_7$.

(*Molecular Weight* = 178·14.)

Pyrosulphuric (or perhaps more correctly *di*-sulphuric) acid appears to be the only true compound of sulphuric acid and its anhydride. This conclusion is borne out by an inspection of the freezing-point curve of oleums of various composition.

Formation.—The methods of formation of the acid are those used for oleum manufacture. On a small scale anhydrous sulphuric acid is mixed with a little more than the correct proportion of anhydride, and the excess of anhydride is removed by standing over anhydrous acid.[1] The β trioxide is found to dissolve extremely slowly.

Properties and Reactions.—The dry acid melts at 35° and in the molten state is very liable to supercooling. The dry crystals have no appreciable vapour tension of trioxide, and can be placed in a stream of dry air without decomposition, but the same treatment of the molten or supercooled liquid decomposes it to some extent. The heat of solution of 1 gram-molecule in 1600 molecules of water is 26·9 kilogram calories,[2] and the specific heat, according to Knietsch, is about 0·36. It is decomposed on heating. Certain metals, including silver and mercury, dissolve in it at its melting-point. Copper gives cuprous sulphide and some sulphate, and tin gives a blue liquid probably containing the oxide S_2O_3.

Weber claimed to have isolated a definite compound $H_2SO_4,3SO_3$, but the existence of this, as of the supposed compound $3H_2SO_4,4SO_3$, has not been confirmed.

The Pyrosulphates.

Before passing to the general properties of oleum, the pyrosulphates will be briefly considered. Representatives of both normal salts, $M_2S_2O_7$, and acid salts, MHS_2O_7, are known.

Formation.—(i) Alkaline pyrosulphates are formed on heating the bisulphates. The evolution of water is said to begin at 300° and to be over at 400°. Baum[3] took out a patent for heating in a vacuum at 260° to 320°. It is probable that the practicability of this process varies greatly with the nature of the base. According to Cambi and Bozza,[4] the most recent investigators in this field, the dehydration is never quite complete, even under reduced pressure or in a current of sulphur trioxide. (ii) Sulphuric anhydride reacts with the

[1] Sckultz-Sellack, *Ber.*, 1871, **4**, 109.
[2] Thomsen, *Ber.*, 1873, **6**, 713.
[3] *Ber.*, 1887, **20**, 752; Germ P. 40696.
[4] *Ann. Chim. applicata*, 1923, **18**, 221.

normal anhydrous sulphates if they are finely ground, or if the reaction is aided by heating. The sulphates of potassium, silver, thallium, and ammonium react easily; sodium sulphate less readily, and the sulphates of the alkaline earths with some difficulty.[1] This is the only method which gives pure salts.[2] (iii) Chlorsulphonic anhydride converts the normal sulphates into pyrosulphates: $SO_3HCl + M_2SO_4 = M_2S_2O_7 + HCl$. This is of more general application than method (i).

Properties and Reactions.—The alkali salts are said to be stable at a mild red heat (the sodium salt is an exception), but decompose on more intense heating, reforming the normal sulphates. They are of varying stability towards water, for the most reacting with it to form bisulphates. Bunsen found the calcium salt most stable in this respect and capable of crystallisation unchanged from a boiling solution.

Potassium Pyrosulphate, obtained by the foregoing methods, consists of transparent prisms of density 2·512 and melting-point 414·2°. At 315° the salt is transformed into an opaque porcelain-like substance.[2] When dissolved in water, cooling due to solution takes place at first, but a few minutes after, heat is evolved on account of the conversion to bisulphate. The heat given out by the reaction $K_2SO_4 + SO_3 \rightarrow K_2S_2O_7$ is 26·1 kilocalories (note that $K_2O + SO_3 \rightarrow K_2SO_4 + 142·4$, the trioxide being solid in each case).[3] It is interesting to observe that Berthelot had to heat his reaction mixture to 180° to obtain this salt by method (ii). The bisulphate KHS_2O_7 can be obtained by crystallising the normal salt from fuming acid. Both this and the normal salt are stable in dry air and neither has an appreciable vapour pressure of trioxide. On standing in an ordinary atmosphere each reverts slowly to bisulphate.

Sodium Pyrosulphate is much more difficult to obtain in a pure state. A mixture of anhydrous sulphate and trioxide gives, at 150°, a fritted mass having almost the composition $Na_2S_2O_7$. Method (iii) in this case gives better results. Powdered dry sulphate is moistened with chlorsulphonic anhydride, and the reaction having ended, the excess of

[1] Schultz, *Ber.*, 1884, **17**, 2705.
[2] Cambi and Bozza, *loc. cit.*
[3] Berthelot, *Ann. Chim. Phys.* [4], **30**, 433.

anhydride is distilled away.[1] Method (ii) can also be used. The pure salt forms lustrous, translucent crystals of density 2·658 and melting-point 400·9°. It dissociates appreciably at 460°.[2] No acid salt is known in this case. The normal salt is instantly converted into bisulphate in contact with water.

Many attempts have been made to obtain sodium pyrosulphate from the bisulphate, which constitutes the greater part of nitre cake, with a view in many cases to obtaining free sulphuric anhydride by a further reaction. The production of pyrosulphate certainly occurs, but is never complete (at the ordinary pressure), for the evolution of water is always accompanied by loss of sulphuric anhydride to a degree which increases as the water is driven out. When bisulphate is heated, the water comes off at first fairly readily, and 50 per cent. of the available water can be removed without reducing by more than 2 or 3 per cent. the free acidity as determined by titration of the dissolved sample. To abstract about 85 per cent. of the water causes a loss in free acidity of about 30 per cent. Attention should, however, be paid to the possibility of working in a vacuum.[3]

Oleum.

Fuming sulphuric acid of any concentration consists of sulphur trioxide in solution with sulphuric acid. There appears to be little evidence of the existence of any other compound, even of pyrosulphuric acid, in any of these mixtures, when they are liquid.

The composition of oleum may be stated in several ways. The method most often adopted here will be to state the percentage of uncombined (free) trioxide. This is not sufficient, however, for purposes of calculation, and either the percentage of total trioxide or the equivalent percentage of sulphuric acid must often be known in addition. Both quantities are given in the first of the two tables in the form of equivalents to all percentages of free trioxide between 0 and 100.

[1] Schultz, *Ber.*, 1884, 17, 2708.

[2] Cambi and Bozza, *loc. cit.*

[3] Baum, *loc. cit.*, and British Cellulose Company, and Bader, B. P. 177310 of 1921.

Calculations of this kind frequently involve ordinary sulphuric acid. A second table is therefore added by which each even half per cent. of H_2SO_4 may be converted to SO_3, or *vice versâ*. This extends the figures from 122·5 per cent. H_2SO_4 to 40 per cent. H_2SO_4.

Composition of Oleum.

Per cent. Free SO_3.	Equivalent Per cent H_2SO_4	Per cent. Total SO_3.	Per cent. Free SO_3.	Equivalent Per cent. H_2SO_4	Per cent. Total SO_3.	Per cent. Free SO_3.	Equivalent Per cent. H_2SO_4.	Per cent. Total SO_3.
0	100·00	81·63	34	107·65	87·88	68	115·30	94·12
1	100·23	81·82	35	107·88	88·06	69	115·53	94·31
2	100·45	82·00	36	108·10	88·25	70	115·75	94·49
3	100·68	82·18	37	108·33	88·43	71	115·98	94·67
4	100·90	82·37	38	108·55	88·61	72	116·20	94·86
5	101·13	82·55	39	108·78	88·80	73	116·43	95·04
6	101·35	82·73	40	109·00	88·98	74	116·65	95·22
7	101·58	82·92	41	109·23	89·16	75	116·88	95·41
8	101·80	83·10	42	109·45	89·35	76	117·10	95·59
9	102·03	83·29	43	109·68	89·53	77	117·33	95·78
10	102·25	83·47	44	109·90	89·71	78	117·55	95·96
11	102·48	83·65	45	110·13	89·90	79	117·78	96·14
12	102·70	83·84	46	110·35	90·08	80	118·00	96·33
13	102·93	84·02	47	110·58	90·27	81	118·23	96·51
14	103·15	84·20	48	110·80	90·45	82	118·45	96·69
15	103·38	84·39	49	111·03	90·63	83	118·68	96·88
16	103·60	84·57	50	111·25	90·82	84	118·90	97·06
17	103·83	84·76	51	111·48	91·00	85	119·13	97·24
18	104·05	84·94	52	111·70	91·18	86	119·35	97·43
19	104·28	85·12	53	111·93	91·37	87	119·58	97·61
20	104·50	85·31	54	112·15	91·55	88	119·80	98·80
21	104·73	85·49	55	112·38	91·73	89	120·03	97·98
22	104·95	85·67	56	112·60	91·92	90	120·25	98·16
23	105·18	85·86	57	112·83	92·10	91	120·48	98·35
24	105·40	86·04	58	113·05	92·29	92	120·70	98·53
25	105·63	86·22	59	113·28	92·47	93	120·93	98·71
26	105·85	86·41	60	113·50	92·65	94	121·15	98·90
27	106·08	86·59	61	113·73	92·84	95	121·38	99·08
28	106·30	86·78	62	113·95	93·02	96	121·60	99·28
29	106·53	86·96	63	114·18	93·20	97	121·83	99·45
30	106·75	87·14	64	114·40	93·39	98	122·05	99·63
31	106·98	87·33	65	114·63	93·57	99	122·28	99·82
32	107·20	87·51	66	114·85	93·76	100	122·50	100·00
33	107·43	87·69	67	115·08	93·94	...	...	...

Problems in relation to mixing oleum with ordinary or fuming sulphuric acid, or to preparing oleum of a given strength, are best facilitated by using the table to obtain the equivalent percentages of sulphuric acid. If an oleum of strength *b* is to be "broken down" to strength *c* by means of an acid of strength

a, then for 1 part of the acid of strength a, x parts of that of strength b must be taken, where

$$\frac{c-a}{b-c}$$

a, b, and c being, of course, in the same units in each case.

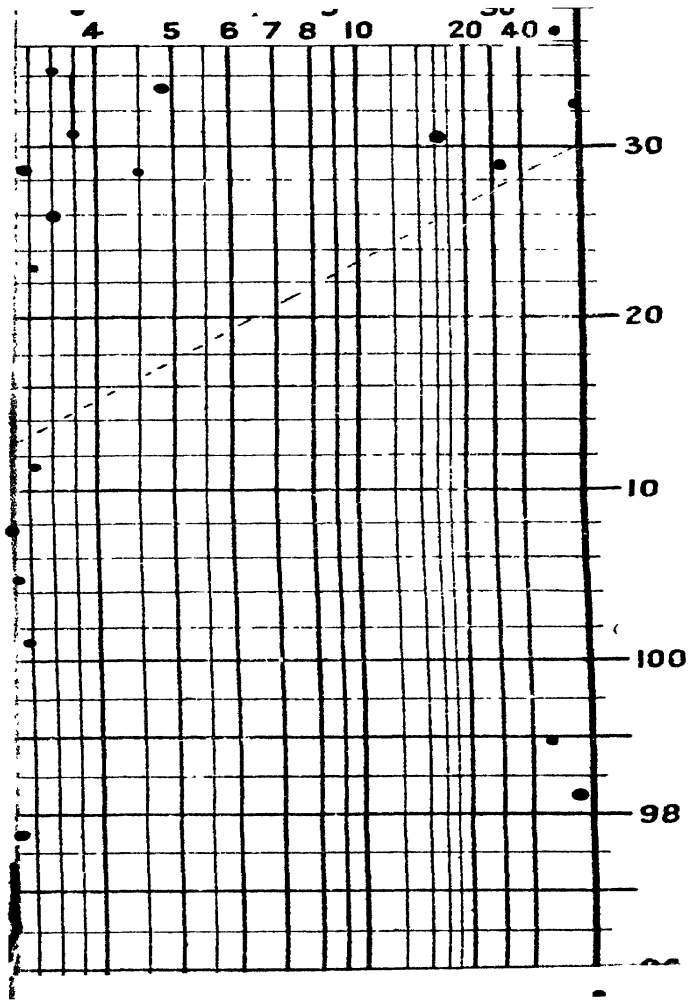
Composition of Sulphuric Acid.

(Condensed table.)

Example.—40 per cent. H_2SO_4 = 32·65 per cent. SO_3; 40 per cent. SO_3 = 49·00 per cent. H_2SO_4.

Per cent. H_2SO_4.	Per cent. SO_3. / Per cent. H_2SO_4.	Per cent. SO_3.	Per cent. H_2SO_4	Per cent. SO_3. / Per cent. H_2SO_4.	Per cent. SO_3.	Per cent. H_2SO_4	Per cent. SO_3. / Per cent. H_2SO_4	Per cent. SO_3.	Per cent. H_2SO_4.	Per cent. SO_3. / Per cent. H_2SO_4	Per cent. SO_3.
49·00	·0·	32·65	67·38	55·	44·90	85·75	70·	57·14	104·18	85·	69·39
49·61	·5	33·06	67·99	·5	45·30	86·36	·5	57·55	104·74	·5	69·79
50·23	41·	33·47	68·60	56·	45·71	86·98	71·	57·96	105·35	86·	70·20
50·84	·5	33·88	69·21	·5	46·12	87·59	·5	58·37	105·96	·5	70·61
51·45	42·	34·28	69·83	57·	46·53	88·20	72·	58·77	106·58	87·	71·02
52·06	·5	34·69	70·44	·5	46·94	88·81	·5	59·18	107·19	·5	71·43
52·68	43·	35·10	71·05	58·	47·35	89·43	73·	59·59	107·80	88·	71·83
53·29	·5	35·51	71·66	·5	47·75	90·04	·5	60·00	108·41	·5	72·24
53·90	44·	35·92	72·28	59·	48·16	90·65	74·	60·41	109·03	89·	72·65
54·51	·5	36·33	72·89	·5	48·57	91·26	·5	60·81	109·64	·5	73·06
55·13	45·	36·73	73·50	60·	48·98	91·88	75·	61·22	110·25	90·	73·47
55·74	·5	37·14	74·11	·5	49·39	92·49	·5	61·63	110·86	·5	73·88
56·35	46·	37·55	74·73	61·	49·79	93·10	76·	62·04	111·48	91·	74·28
56·96	·5	37·96	75·34	·5	50·20	93·71	·5	62·45	112·09	·5	74·69
57·58	47·	38·37	75·95	62·	50·61	94·33	77·	62·86	112·70	92·	75·10
58·19	·5	38·77	76·56	·5	51·02	94·94	·5	63·26	113·31	·5	75·51
58·80	48·	39·18	77·18	63·	51·43	95·55	78·	63·67	113·93	93·	75·92
59·41	·5	39·59	77·79	·5	51·84	96·16	·5	64·08	114·54	·5	76·32
60·03	49·	40·00	78·40	64·	52·24	96·78	79·	64·49	115·15	94·	76·73
60·64	·5	40·41	79·01	·5	52·65	97·39	·5	64·90	115·76	·5	77·14
61·25	50·	40·82	79·63	65·	53·06	98·00	80·	65·30	116·38	95·	77·55
61·86	·5	41·22	80·24	·5	53·47	98·61	·5	65·71	116·99	·5	77·96
62·48	51·	41·63	80·85	66·	53·88	99·23	81·	66·12	117·60	96·	78·36
63·09	·5	42·04	81·46	·5	54·28	99·84	·5	66·53	118·21	·5	78·77
63·70	52·	42·45	82·08	67·	54·69	100·45	82·	66·94	118·83	97·	79·18
64·31	·5	42·86	82·69	·5	55·10	101·06	·5	67·34	119·44	·5	79·59
64·93	53·	43·26	83·30	68·	55·51	101·68	83·	67·75	120·05	98·	80·00
65·54	·5	43·67	83·91	·5	55·92	102·29	·5	68·16	120·66	·5	80·41
66·15	54·	44·08	84·53	69·	56·32	102·90	84·	68·57	121·28	99·	80·81
66·76	·5	44·49	85·14	·5	56·73	103·51	·5	68·98	121·89	·5	81·22

If this kind of calculation has to be carried out very frequently, and if, as generally occurs in technical work, the acids to be mixed have compositions lying each within fairly narrow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limits, some kind of graphical chart saves a great deal of arithmetical labour, and gives results which are sufficiently accurate for many purposes. The alignment chart lends itself readily to this calculation, and the example given in Fig. 2 may prove useful; by its means most of the arithmetical problems involved in mixing oleum and sulphuric acid can be solved immediately, almost by inspection. The method of construction is noted[1] and the chart can be reconstructed to cover almost any range of this, or a similar calculation. Suppose that we desire to obtain acid of 96·7 per cent. by mixing two acids of 90 per cent. H_2SO_4 (*a*) and of 30 per cent. free trioxide (*b*). A thread is held stretched over these two points on the vertical axes, and the point of intersection of the horizontal line from 96·7 with the line of the thread is found by the eye. The vertical line passing through this point gives, on the scale at the base, the required ratio. In this case 0·67 part of the strong acid are required for one of the weak. The dotted lines on the chart illustrate this example. Other uses will readily suggest themselves.

There are two varieties of oleum which are principally used in industry, containing approximately 20 per cent. and 66 per cent. of free trioxide. The first is largely made and used in explosives works. The second is required mainly for the sulphonation of organic compounds, and is therefore common in the dye and intermediate industry. Each variety is distinguished by a composition lying very close to a minimum of the freezing-point curve. To depart far from these two concentrations is to obtain an oleum which cannot be kept liquid without heating.

The acid containing 60 to 70 per cent. of free trioxide is prepared by distillation of oleum of lower strength, for there is a limit to the concentration which can be reached directly in a contact plant. This distillation is conducted in fire-heated steel vessels, the sulphur trioxide being driven over into a water-

[1] This is an alignment chart extended to allow of four variables instead of three. *Construction*: *a* and *b* are set off to the *same* scale on the two axes. The two scales must be level, *i.e.*, any horizontal line must have the same number at each end. The vertical lines are drawn through points where the base line has been divided (preferably homographically), so that each graduation gives the ratio of the segment of the base to the other.

cooled receiver (sometimes fitted with a stirrer) containing a small quantity of acid, or of the oleum of the kind being distilled. A special form of still made by a German firm for this work is shown in Fig. 3.

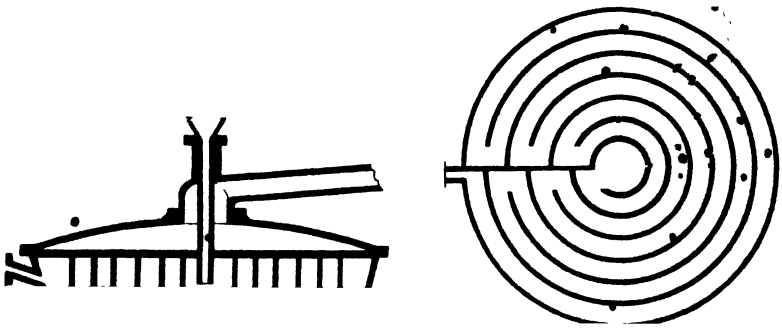


FIG. 3.

The Physical Properties of Oleum.

For information on the physical properties of oleum we are largely indebted to Knietsch, whose lecture in 1901[1] let in a flood of light on this field for the first time. The extensive and very various data obtained by him and his co-workers were probably gathered with a view to approximate technical, as distinct from exact scientific application, and in the main they have served this purpose well. It is necessary to emphasise, however, what has many times been pointed out—that they should be accepted, for any purpose, only after careful inspection, and with considerable reserve. The figures given have often been found difficult to reproduce by other workers, and are occasionally discordant among themselves. The actual experimental figures are not always given, and the methods of interpolation used to obtain the results are not described. In one case the data cannot be reduced to any specific basis.

Specific Gravity.—The following series of specific gravities is due to Winkler, and was obtained for oleum made by the old Nordhausen process, and therefore not likely to be very pure:—

[1] *Ber.*, 1901, [illegible], 4069-4115.

Free SO_3 per cent.	Specific Gravity at 20°.	Free SO_3 per cent.	Specific Gravity at 20°.	Free SO_3 per cent.	Specific Gravity at 20°.
1·5	1·860	10·1	1·900	28·0	1·940
2·7	1·865	10·6	1·905	29·9	1·945
4·3	1·870	11·4	1·910	31·5	1·950
5·4	1·875	13·3	1·913	32·8	1·955
6·4	1·880	16·0	1·920	35·9	1·960
7·3	1·885	18·7	1·925	39·7	1·965
8·2	1·890	21·3	1·930	44·6	1·970
9·3	1·895	25·7	1·935		

Messel[1] gave the following values for 26·6°, and also those calculated for 15·5° :—

Specimens.	Percentage of SO_3.	Specific Gravities. At 80° F. (= 26·6° C.)	Specific Gravities. Calculated for 60° F. (= 15·5° C.)
Liquid	8·3	1·842	1·852
„	30·0	1·930	1·940
Crystalline mass, resembling nitre	40·0	1·956	1·970
„ „	44·5	1·961	1·975
„ „	46·2	1·963	1·977
„ „	59·4	1·980	1·994
Liquid	60·8	1·992	2·006
„	65·0	1·992	2·006
„	69·4	2·002	2·016
Crystallised	72·8	1·984	1·988
„	80·0	1·959	1·973
„	82·0	1·953	1·967

These relate to commercial acids made by the contact process as also do the figures given by Knietsch for 15°, 35°, and 45°.

Specific Gravities of Oleum at 15° *and* 45°.

Free SO_3 per cent.	Specific Gravity at 15° C.	Specific Gravity at 45° C.
0·0	1·8500	1·822
10·0	1·888	1·858
20·0	1·920	1·887
30·0	1·957	1·920
40·0	1·979	1·945
50·0	2·009	1·964 max.
60·0	2·020 max.	1·959
70·0	2·018	1·942
80·0	2·008	1·890
90·0	1·990	1·864
100·0	1·984	1·814

[1] *J. Soc. Chem. Ind.*, 1885, 4, 573.

Specific Gravities of Oleum at 35° C.

Total SO_3 per cent.	Free SO_3 per cent.	Specific Gravity.	Total SO_3 per cent.	Free SO_3 per cent.	Specific Gravity.
81·63	0	1·8186	91·18	52	1·9749
81·99	2	1·8270	91·55	54	1·9760
82·36	4	1·8360	91·91	56	1·9772
82·73	6	1·8425	92·28	58	1·9754
83·09	8	1·8498	92·65	60	1·9738
83·46	10	1·8565	93·02	62	1·9709
83·82	12	1·8627	93·38	64	1·9672
84·20	14	1·8692	93·75	66	1·9636
84·56	16	1·8756	94·11	68	1·9600
84·92	18	1·8830	94·48	70	1·9564
85·30	20	1·8919	94·85	72	1·9502
85·66	22	1·9020	95·21	74	1·9442
86·03	24	1·9092	95·58	76	1·9379
86·40	26	1·9158	95·95	78	1·9315
86·76	28	1·9220	96·32	80	1·9251
87·14	30	1·9280	96·69	82	1·9183
87·50	32	1·9338	97·05	84	1·9115
87·87	34	1·9405	97·45	86	1·9046
88·24	36	1·9474	97·78	88	1·8980
88·60	38	1·9534	98·16	90	1·8888
88·97	40	1·9584	98·53	92	1·8860
89·33	42	1·9612	98·90	94	1·8712
89·70	44	1·9643	99·26	96	1·8605
90·07	46	1·9672	99·63	98	1·8488
90·44	48	1·9702	100·00	100	1·8370
90·81	50	1·9733	...	...	...

The data of the last two tables are apparently based on the density of water at 15°, taken as unity. It will be noticed that the various sets of data are by no means concordant. This is very probably due to the varying nature and quantity of impurity present in commercial acids, and it is always preferable that a works should carry out these determinations for itself with the accuracy sufficient for the purpose for which they are required. The published tables are rarely found to be in agreement with such determinations, and it would appear that many of the figures given by Knietsch are too high. The following, for instance, were obtained at Gretna in 1917 by J. C. C. Taylor :—

Sp. gr. at 15° . .	1·8955	1·9008	1·9055	1·9110	1·916c
Free SO_3 per cent. .	18	19	20	21	22

To correct for temperature difference from 15°, for every degree of such difference between :—

10° and 20°, subtract 0·0015
20° „ 55°, „ 0·0010
55° „ 60°, „ 0·0020

These figures are lower than those given by Knietsch. The oleum examined had been obtained from sulphuric acid recovered from nitro-glycerine and nitro-cotton manufacture.

Another series which are in use in a large explosive works for plant control may also be given.

Specific Gravities of 20 *per cent. and* 10 *per cent. Oleum.*

Temperature.	20 per cent. Oleum.	10 per cent. Oleum.	Temperature.	20 per cent. Oleum.	10 per cent. Oleum.
10°	1·912	1·880	40°	1·877	1·850
15°	1·905	1·875	45°	1·872	1·845
20°	1·897	1·870	50°	1·867	1·840
25°	1·887	1·865	55°	1·862	1·835
30°	1·887	1·860	60°	1·857	1·830
35°	1·882	1·855	...	...	...

These, again, are all lower than Knietsch's figures.

It will be noticed that from the minimum slightly below 100 per cent. H_2SO_4, the density increases continuously until a maximum is reached, the position of which varies somewhat with temperature. At 35° the maximum value is 1·9772 for 56 per cent. of free trioxide. From this point the density sinks until pure trioxide is reached—according to Knietsch 1·984 at 15°. All of Knietsch's determinations for the trioxide are discordant with the more recent determinations of the density of this substance by Lichty.

Melting-point.—The melting-points of a series of oleums were determined by Knietsch. The method adopted is best given in his own words. "That temperature was first observed, to which the acid could be cooled, with stirring, without solidifying. As soon as the first crystals formed the vessel was taken out of the cooling bath, and, stirring being continued, the highest temperature was observed to which the thermometer rose, which remained constant on further solidification of the liquid." (This temperature is given as the melting-point.) "The crystals were then melted by careful warming and the temperature observed at which the last residue melted." The last temperature observed in this way (but not recorded by Knietsch except in the form of a dotted line on his graph) is the final melting-point, and is probably not far from the

initial freezing-point; but the temperature taken as the melting-point, for which the results are given, lies considerably lower in each case and is neither the initial nor the final freezing-point, but an intermediate temperature. The results although of not very certain significance are of practical value and in extended use, and are given below as taken from the paper. The only temperatures, however, which appear to correspond to reproducible phenomena, are those represented by the upper dotted line on Knietsch's graph, *i.e.*, probably the *liquidus* curve. They are due to interpolation of a curve drawn from the experimental results.

Melting-Point of Oleum.

Per cent. Free SO_3.	Melting-point	Per cent. Free SO_3.	Melting-point.	Per cent. Free SO_3.	Melting-point.
0	+ 10·0	35	+ 26·0	70	+ 9·0
5	+ 3·5	40	33·8	75	17·2
10	− 4·8	45	34·8	80	22·0
15	− 11·2	50	28·5	85	33·0 (27·0)
20	− 11·0	55	18·4	90	34·0 (27·7)
25	− 0·6	60	+ 0·7	95	36·0 (26·0)
30	+ 15·2	65	+ 0·8	100	40·0 (17·7)
0·0	+ 10·0	34·7	+ 26·0	72·8	14·8
2·0	+ 8·2	40·1	34·2	78·3	20·3
7·5	− 0·8	45·6	34·2	83·7	29·2
12·9	− 9·2	51·0	25·8	89·1	33·8
18·3	11·0	56·4	14·2	94·6	36·0
23·8	− 2·2	61·9	0·8	100·0	40·0
29·2	+ 13·5	67·3	4·5	...	...

The course of the curve is shown in Fig. 4. There is a minimum at from 15 to 20 per cent. Oleum of this concentration is unlikely to freeze on the coldest days in this country. The curve then tends upward to a maximum, the position of which corresponds almost exactly to the formula of pyrosulphuric acid—$H_2S_2O_7$. Falling from this, another minimum is reached at 60 to 65 per cent.—the usual composition of the concentrated commercial oleum—and from these the curve rises again until pure trioxide is reached. Before doing so, however, it divides into two branches. The lower one (to which the bracketed figures in the table relate) refers to freshly prepared oleum which has not yet had time to polymerise. Very concentrated

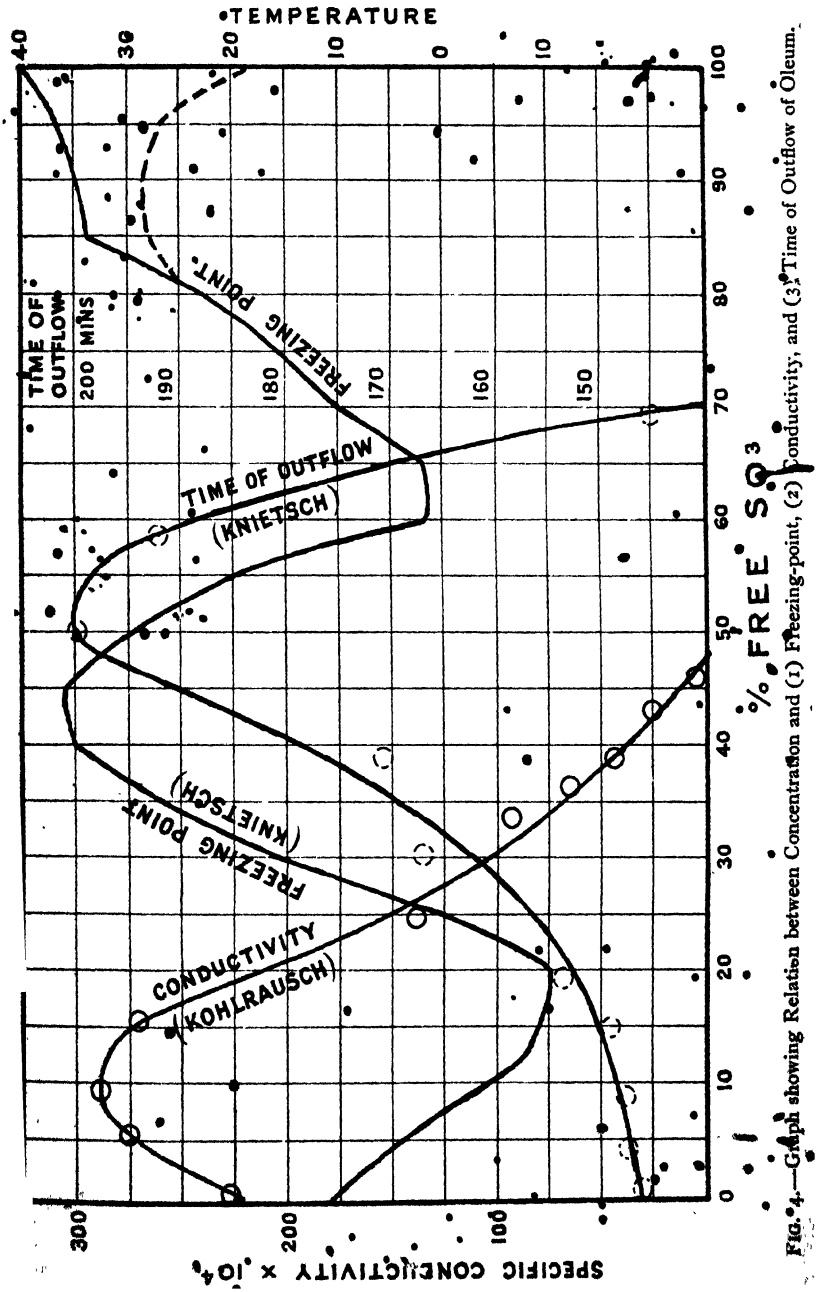


FIG. 4.—Graph showing Relation between Concentration and (1) Freezing-point, (2) Conductivity, and (3) Time of Outflow of Oleum.

oleum of 85 per cent. or more is practically a solution of sulphuric acid in the trioxide, and consequently undergoes the α-β change on standing; and if the change is allowed to proceed to completion the oleum may not even melt on being heated, but only lose trioxide by sublimation.

It will be noticed that the first minimum on the curve occurs at about the same concentration—15 to 20 per cent. of trioxide—as does the maximum of electrical conductivity. We do not certainly know that the acids of this and the other minimum melting-point (60 to 65 per cent. trioxide) form simple eutectics when they solidify, but some general conclusions relating to the composition of the solids first crystallising from various acids may be drawn. From weak oleums—0 to 15 per cent.—pure sulphuric acid must be the first solid to crystallise on cooling, to be followed later at the temperature of the minimum by a mixture of this acid and pyrosulphuric acid. An acid between 20 and 45 per cent. will first deposit mainly pyrosulphuric acid, and then, in the measure of the amount by which its initial concentration is lower than 45 per cent.—a mixture of the same composition as before. Acid of a composition lying at the summit of the curve should solidify almost entirely at constant temperature, and the first and last fractions should not vary greatly in composition. The same argument may be applied to the region of the curve beyond 45 per cent. Stronger acids must deposit pyrosulphuric acid as before, but what composition the mixture freezing at the second minimum point may have is a question which, in the present state of our knowledge, is not easy to answer exactly.

Specific Heat.[1]—One kilogram of the oleum was heated and allowed to cool to 35° in a glass flask, and the flask was then plunged into 2 kilograms of water. The oleum was allowed to cool to 25°, and the flask was then removed quickly from the bath, the rise of temperature of the bath being noted.

Boiling-point.[1]—The boiling-point was taken to be the temperature, indicated by a thermometer dipping into the liquid, at which ebullition of the liquid *first* took place. If the boiling is conducted with a reflux cooler somewhat higher values are obtained.

Vapour Pressure.[1]—"The usual barometric method could

[1] Knietsch.

Specific Heat of Oleum, 25° *to* 35°

Per cent. Free SO_3.	Per cent. Total SO_3.	Specific Heat.	Per cent. Free SO_3.	Per cent. Total SO_3.	Specific Heat.
...	76·8	0·3691*	51·0	91	0·370
...	78·4	0·3574*	56·45	92	0·400
...	80	0·350	61·89	93	0·425
...	80·0	0·3574*	63·5	93·3	0·4325*
...	81·5	0·3478*	67·34	94	0·455
2·0	82	0·345	70·6	94·64	0·4730*
10·0	83·46	0·3417*	72·78	95	0·495
12·89	84	0·340	78·23	96	0·535
20·95	85·48	0·3391*	81·0	96·52	0·5598*
23·88	86	0·340	83·67	97	0·590
29·74	87·13	0·3392*	88·6	97·92	0·6526*
34·67	88	0·350	89·12	99	0·650
38·75	88·75	0·3498*	94·56	99	0·710
45·56	90	0·360	98·9	99·8	0·7413*
46·1	90·1	0·3599*	100·0	100	0·770
49·4	90·73	0·3660*	...	...	...

Boiling-Point of Oleum.

Per cent. Free SO_3.	Per cent. Total SO_3.	Boiling-point °C.	Barometric pressure, mm.
3·64	82·3	212	759
9·63	83·4	170	759
26·23	86·45	125	759
42·84	89·5	92	759
63·20	93·24	60	759
97·2	99·5	43	759

Vapour Pressure in Atmospheres.

($\frac{3}{4}$ vol. Oleum + $\frac{1}{4}$ vol. Air.)

t° C.	30 per cent. SO_3.	40 per cent. SO_3.	50 per cent. SO_3.	60 per cent. SO_3.	70 per cent. SO_3.	80 per cent. SO_3.	100 per cent. SO_3.
35	...	...	...	...	...	0·150	0·400
40	...	0·075	...	0·225	0·375	0·500	0·650
45	0·050	0·125	...	0·350	0·575	0·650	0·875
50	0·100	0·175	0·350	0·525	0·775	0·875	1·200
55	0·140	0·225	0·450	0·675	1·025	1·200	1·600
60	0·200	0·275	0·550	0·825	1·400	1·500	1·850
65	0·225	0·350	0·700	1·025	1·650	1·900	2·250
70	0·275	0·400	0·825	1·275	2·050	2·300	2·725
75	0·340	0·475	1·000	1·570	2·525	2·800	3·300
80	0·400	0·575	1·150	1·850	3·100	3·500	4·000
85	0·490	0·675	1·400	2·150	3·700	4·175	4·900
90	0·530	0·825	1·700	2·575	4·400	5·050	5·900
95	0·625	0·950	2·050	3·150	5·200	6·000	...
100	0·730	1·100	2·400	3·700	6·000	...	...

The asterisks indicate the experimental results; other values have been obtained by graphic interpolation from them.

not be used in the case on account of the chemical action of the trioxide on the mercury, and the measurements were therefore made in an iron apparatus by means of a manometer which seemed sufficiently accurate for practical purposes.

The above are "smoothed" data. Knietsch gives no experimental results. Though useful possibly for practical purposes these values must be accepted with considerable reserve, for it has been shown that they lead to impossible values of the latent heat of vaporisation of sulphur trioxide.[1] The data in this table begin where those of most use would end, and extrapolation of the curves connecting per cent. of free trioxide and vapour pressure cannot be carried out at lower temperatures on account of the omission of most of the essential values, and appears to be of little value at higher temperatures. At 98·5 per cent. H_2SO_4, the vapour tension is known to be practically zero, but the curves, when produced in any regular way, do not indicate this.

A series of measurements of the vapour pressure of the full trioxide in oleum has recently been made by M'David[2] (*J. Soc. Chem. Ind. Trans.* 1924, **43**, 57) by the dynamic method. Mixtures of purified burner-gas and air were dried and passed over a catalyst which converted the sulphur dioxide to trioxide to the extent of about 98 per cent. The converted gas was passed into a small wash-bottle containing oleum and placed in a thermostat. The percentage of sulphur dioxide was maintained as constant as possible and was checked frequently by analysis. The amount of unconverted dioxide also being estimated, from these data and from the analysis of the acid when equilibrium had been attained at any particular temperature, the partial pressure of the trioxide in the gas-mixture could be obtained. The vapour pressure of the oleum is equal to this quantity. The experimental results are given in the table on page 53, and in graphical form in Fig. 5.

It will be noticed that in Fig. 5 a number of heavy horizontal lines have been drawn to indicate certain percentages of sulphur trioxide in the gas which is in equilibrium, in regard to trioxide, with oleum. These lines constitute a scale by means of which it is easy to determine the greatest

[1] Porter, *Trans. Faraday Soc.*, 1917, **13**, 399.

[2] Thanks are due to Dr J. W. M'David for making possible the inclusion of these results by supplying a copy of his paper in advance.

concentration of oleum it is possible to obtain by absorption from any given gas mixture. This aspect of the matter will be discussed in detail in Chapter VII. Attention should be given to the great influence of temperature which the graphs indicate. On the average, a vapour pressure which is higher than 20 mm. is doubled by a rise of temperature of 10°.

Vapour Pressure of Oleum

(In mm. of Mercury).

t°C.	Per cent. Free SO_3.	mm.	Per cent. Free SO_3.	mm.	Per cent. Free SO_3.	mm.	Per cent. Free SO_3.	mm.	Per cent. Free SO_3.	mm.
40°	20·6	6·1	27·8	11·4	34·9	22·0	39·6	38·9	42·6	51·9
50°	16·7	5·5	24·0	10·9	30·3	23·6	35·3	39·1	37·1	51·2
60°	14·9	5·5	21·2	12·9	26·3	24·1	31·0	38·5	32·9	50·5
70°	9·1	5·3	16·6	11·5	21·1	23·6	24·4	39·5	28·5	50·9
80°	...	...	11·2	11·4	13·5	23·4	16·3	37·7	20·4	50·4
90°	...	...	4·5	11·4	8·0	23·4	10·4	37·4	14·0	51·2

Electric Conductivity.—Reliable measurements of the specific electric conductivity are those made by Kohlrausch at 18°.[1] They extend to 111 per cent. of sulphuric acid and are given in the table below. Since it is useful to have the conductivities of the stronger sulphuric acids also, a selection of these is included. The fourth column contains the temperature

Specific Electric Conductivity at 18 (k_{18}).

Per cent. Free SO_3.	Per cent. H_2SO_4.	$k_{18}\times10^4$.	c.	Per cent. Free SO_3.	Per cent. H_2SO_4.	$k_{18}\times10^4$.	c.
...	90	1075	0·032	5·0	101·12	269	0·031
...	92	1102	0·030	5·8	101·30	275	0·031
...	94	1071	0·028	9·2	102·08	289	0·031
...	96	938	0·025	15·7	103·53	271	0·032
...	96·87	845	0·028	24·9	105·61	138	...
...	98·42	592	0·027	33·8	107·61	93	0·039
...	99·08	361	0·028	36·4	108·16	65	0·040
...	99·44	213	0·028	39·0	108·78	43	0·048
...	99·75	80	0·040	40·9	109·20	35	0·050
...	99·98	157	0·031	43·2	109·74	25	0·054
0·6	100·14	187	0·030	44·6	110·04	19	0·054
0·9	100·21	199	0·030	46·1	110·38	14	0·056
2·3	100·51	227	0·032	49·8	111·2	8	0·061

these is included. The fourth column contains the temperature

[1] *Leitvermögen der Elektrolyte*, Teubner, Leipzig, 1898, 156.

coefficients which (c) by the conductivity (k_t) at any temperature (t) between 18° and 26° (or with less accuracy, at a higher temperature) may be calculated as:—

$$k_t = k_{18}\{1 + c(t - 18)\}$$

The course of these figures is shown in Fig. 4. The conductivity of oleum rises until a maximum is reached at about 10 per cent. of free trioxide and then falls off with increasing concentration.

Another series of determinations extending to 90 per cent. of free trioxide was made by Knietsch. His cell consisted of a cylindrical glass vessel having its axis vertical. In it were placed, in parallel vertical planes 1·5 cm. apart, two platinum electrodes in the form of discs 4 cm. in diameter. It is stated that 0·02 ohm could be measured with exactness, but the constant of the cell is omitted, and it is not possible to calculate the specific conductivity from the experimental data in any certain way. These data are given below. The

Electrical Resistance at 25°.

Per cent. Free SO_3.	Per cent. Total SO_3.	Ohms.	Per cent. Free SO_3.	Per cent. Total SO_3.	Ohms.
0·34	81·70	6·15	45·0	90·5	23·4
0·5	81·74	5·35	50·0	90·8	53·0
4·0	82·4	2·43	54·0	91·6	88·0
9·8	83·4	2·20	60·3	92·7	220
14·0	84·2	2·15 M.	64·0	93·4	287
16·7	84·7	2·15 M.	69·6	94·4	759
19·4	85·2	2·23	75·0	95·4	1265
25·5	86·3	2·95	80·0	96·35	4000 (27°)
29·5	87·1	4·05	83·0	96·9	6650 (32°)
36·3	88·3	6·65	90·0	98·2	61850 (36°)
40·2	89·0	15·2	...	...	...

conductivity rises until a maximum is reached at 16 per cent., and then falls away to a value which is extremely small for 100 per cent. trioxide. The discordance between the curves representing Knietsch's and Kohlrausch's results is very marked; the maximum does not occur on both at the same concentration. This point is of some importance in connection with the rates of corrosion of metals—particularly iron and steel—by oleum of various concentrations, for these rates are almost certainly connected with the conductivities of the acids employed.

Velocity of Outflow.[1]—The acid was drawn up into a 320 c.c. cylindrical vessel of 2·8 cm. diameter to a definite mark, and was then allowed to flow out through a short opening $1\frac{3}{4}$ mm. wide. The time of outflow was recorded. The values given are calculated on the basis—water = 100.

Time of Outflow at 23°.

(Seconds.)

Per cent. Free SO_3.	Time.	Per cent. Free SO_3.	Time.	Per cent. Free SO_3.	Time.
0·9	145·7	30·3	166·9	69·5	145·0
4·2	147·0	39·0	170·8	80·4	125·8
8·5	147·7	49·9	198·7	89·1	109·9
15·1	151·0	58·6	192·0	98·9	100·7
19·4	155·6	...	...	...	...

These figures are shown graphically in Fig. 4. Oleum of 50 per cent. is the most viscous of the series, and requires twice the time to run out that water does. Increase in the trioxide percentage causes an increase in fluidity, and the pure trioxide is practically as fluid as water. It will be noticed that the composition of maximum viscosity is not far removed from that of maximum melting-point and of pyrosulphuric acid.

Capillarity.[1]—The height of capillary ascent was measured in a thermometer capillary with both the dry and the wetted tube. The two observations usually agreed, if not the second was accepted. The tube had a lens-shaped lumen, and 1 mm. length of the tube held 0·122 cub. mm. of mercury. The data given are those calculated on the same basis as before, *i.e.* that water = 100. (The actual rise of water in the tube is given as 85 mm.)

Height of Capillary Rise at 22°.

(Water = 100.)

Per cent. Free SO_3.	Rise in mm.	Per cent. Free SO_3.	Rise in mm.	Per cent. Free SO_3.	Rise in mm.
0·9	38·23	30·3	36·47	69·5	29·41
4·2	38·23	39·0	35·29	80·4	25·88
8·5	37·64	49·9	35·29	89·1	24·70
15·1	37·64	58·6	32·94	98·9	23·52
19·4	36·47	...	...	...	...

There is a fairly sharp inflexion of the curve at about 50 per cent. of trioxide.

Heat of Solution.[1]—The calorimeter held 5 to 6 litres of water. From 40 to 50 gm. of the oleum was allowed to run in from the capillary outlet of a glass bulb, and then the glass was broken and thrown in. The highest temperature attained was noted on a Beckmann thermometer, and the usual corrections were made for radiation. The determinations were also made on a large scale, with a wooden cask holding 400 litres, placed on an accurate weigh-bridge. About 4·2 kilos of acid was used in these experiments. The results agreed well and were given together.

The experimental values are recorded and also "smoothed" values, but it is not clear on what principle the smoothing has been carried out. Porter[2] has examined these data and drawn smooth curves, and his results may be given below. Knietsch worked with both liquid and solid oleum, so that a comparison allows of the deduction of the latent heat of fusion of the trioxide.

Heat of Solution of 1 *gm. of Oleum* (*Calories*).
(Water in large excess.)

Per cent. Free SO_3.	Per cent. Total SO_3.	Heat of Solution.		Latent Heat of Fusion.
		Liquid.	Solid.	
45·6	90	317	294	25
56·4	92	349	325	26
67·3	94	382	359	24
78·3	96	419	395	25
89·1	98	459	437	23
100	100	504	482	22

Average, 24·2

From these can be worked out the heat of solution of trioxide with any given amount of water. This can be specified either as the heat set free when 1 gm. trioxide is diluted with M gm. water (h), or as the heat set free when 1 gm. water is diluted with n gm. trioxide (k). The former specification is in some ways more useful for the present purpose. Values of h and k derived from the figures of the preceding table are given

[1] Knietsch. [2] *Loc. cit.*

below, together with the composition of the acid resulting from the mixture:—

Heat of Mixture of (Liquid) Sulphur Trioxide and Water.

Per cent. Total SO_3.	*h*.	*k*.
81·63	275	1222
85·00	223	1263
90·00	152	1368
95·00	83	1577
100·00	0	Indeterminate

If, for instance, 1 gm. water is diluted with sufficient trioxide (*m* gm.) to bring the composition of the mixture to 90 per cent. total SO_3, 1368 calories will be liberated. The applicability of these figures is of course limited to the ordinary temperature; but as the specific heats are known, the variation with temperature may be found by means of the relation; $\frac{\delta u}{\delta t}$ = difference of thermal capacity of mixture before and after mixing. The quantity *u* refers to 1 gm. of mixture; *k* to 1 gm. of water. Therefore dk/dt is readily obtainable and is given in the following table for various values of *m*:—

Per cent. Total SO_3.	$m = SO_3$ per gm. H_2O.	Thermal Capacity per gram Mixture.		Difference.	$\frac{dk}{dt}$
		Before.	After.		
81·63	4·43	0·345	0·812	0·467	2·536
90·00	9·00	0·375	0·793	0·418	4·180
95·00	19·00	0·510	0·781	0·271	5·420
98·00	49·00	0·650	0·775	0·125	6·120
100·00	Inf.	0·770	0·770	0·00	Ind.

Hence we have at different temperatures for an amount of final solution containing 1 gm. H_2O, the following equations for k_t:—

Per cent. Total SO_3.	k_t in Calories.
81·63	$1·222 + 2·54\,(t - 18°$
85·00	$1·263 + 3·16\,(t - 18°$
90·00	$1·368 + 4·18\,(t - 18°$
95·00	$1·577 + 5·42\,(t - 18°$
98·00	$1·715 + 6·12\,(t - 18°$

The Action of Oleum on Metals.

Iron and Steel.—The corrosion of cast-iron by oleum is in general less than that of iron or mild steel. Knietsch gave the following figures as the results of experiments made by immersing small pieces of cast-iron, mild steel, and wrought-iron in acid for seventy-two hours at 18° to 20°. They are expressed as grams dissolved from 1 square metre per hour:—

Acid.	Cast-Iron.	Mild Steel.	Wrought-Iron.
100 per cent. H_2SO_4	0·087	0·088	0·076
0·91 SO_3	0·201	0·393	0·323
2·0	0·190	0·285	0·514
3·6	0·132	0·441	0·687
4·7	0·154	0·956	1·075
9·5	0·151	0·566	1·321
10·2	0·079	0·758	1·540
12·9	0·270	1·024	0·892
16·2	0·271	1·400	1·530
16·3	0·076	1·988	1·530
23·8	0·070	0·245	0·471
34·7	0·043	0·033	0·053
45·6	0·040	0·018	0·019
Composition	C = 3·55 Graphite = 2·79	C = 0·115	C = 0·076.

A glance at the conductivity curve shows that oleum, after the minimum corresponding to 100 per cent. H_2SO_4, again becomes a good conductor, the maximum conductivity being at about 10 per cent. of trioxide.[1] The corrosion of steel and wrought-iron follows a somewhat similar course. In 27 per cent. oleum iron is said to become almost completely passive, and can be used in contact with the liquid for many years without showing appreciable attack. On this result was based one of the *Badische* patents for making oleum completely free from iron by maintaining the absorbing oleum at about this strength (B. P. 1904 of 1901). Practical experience accords with these statements, and it is found that the liability to corrosion is found to be greatest at strengths intermediate between 20 per cent. oleum and 98 per cent. acid; oleum of from 3 to 12 per cent. has a marked corrosive action, and the activity becomes very

[1] Kohlrausch; 15 to 16 per cent. according to Kneitsch.

small as 23 or 25 per cent. is reached. But temperature is probably more important than concentration.

With cast-iron the phenomena are different, for although the liability to corrosion is less, vessels of this metal are very liable to crack. The greater the amount of graphite the less stable is the iron to the action of the oleum, which eats its way between the crystal faces by oxidising the graphite which exists in thin layers between them. Various gases are generated under high pressure and ferrous sulphate may also crystallise out, and the result is a strain which the metal is unable to withstand. Sulphur dioxide or hydrogen sulphide can sometimes be recognised by the smell on breaking a cracked section. Cast-iron pipes conveying gas containing sulphur trioxide are liable to fail in the same way, often with an almost explosive report. For this reason steel pipes and tanks are always preferred for oleum, cast-iron being more suitable for acid of 98 or 100 per cent.

Lead.—It is well known that sulphuric acid of from 95 to 100 per cent. attacks lead more rapidly as its concentration increases, and that the solubility of lead sulphate in the acid increases in the same sense. These relations are continued into the oleum region, and oleum in general very rapidly destroys lead. The following figures are results of corrosion experiments made by Lunge and Schmidt.[1] Weighed specimens of pure soft lead were immersed at 50° in a special apparatus from which no trioxide could escape as fume. After an exposure of ten hours the specimens were again weighed :—

Corrosion of Lead by Sulphuric Acid and Oleum at 50°.

Per cent. H_2SO_4	96·6	98·85	100	–	–	–	–	–
Free SO_3 per cent	–	–	–	10·1	20·2	29·8	39·7	45·0
Corrosion . .	100	1356	2031	2968	3207	3139	2815	2578

The actual loss in weight in 96·6 per cent. acid was 64·0 grms. per sq. m.

The most complete data for the solubility of lead sulphate

[1] *J. Soc. Chem. Ind.*, 1892, **12**, 146.

in sulphuric acid are those of Ditz and Kaphaüser given in the table below. The basis of calculation is: gms., lead sulphate dissolved *by* 100 gms. of acid of the concentration given.

Solubility of Lead Sulphate in Sulphuric Acid and Oleum.

Per cent. H_2SO_4.	Gms. $PbSO_4$.	Per cent H_2SO_4	Gms. $PbSO_4$.	Per cent. SO_3.	Gms. $PbSO_4$.	Per cent. SO_3.	Gms. $PbSO_4$.
91·3	0·047	98·1	0·54	0·04	4·2	6·4	3·8
93·8	0·063	98·4	0·70	0·9	4·0	11·1	6·0
96·0	0·147	98·6	1·29	2·2	3·6	15·1	7·2
97·0	0·210	98·9	1·34	5·0	3·5	22·4	8·2

There is a slow rise to 97 per cent., and then a rapid one to 100 per cent. Shortly after this the increase becomes even more rapid, and oleum of 20 per cent. can hold about 8 per cent. of its weight of lead sulphate.[1] The general connection between those results and those of Lunge and Schmidt is obvious.

The Analysis of Oleum.

Although other tests are often carried out (among which that for arsenic is the most usual) the estimation most frequently made is that of the total acidity. Acid impurities in oleum are generally very small in amount, so that the results of such estimations are very nearly correct indications of the amount of free trioxide, and by means of special tests for such impurities as sulphur dioxide may be made still more exact. Much has been written on the subject and very various methods are in general use, for the problem may be attacked on two sides, each of which has particular advantages, and the available methods may be divided into two classes: (i) Those depending on direct estimation of total acidity; (ii) Those which estimate the free trioxide by either chemical or physical methods.

The taking of the sample is not a simple task. Measurement in a pipette is out of the question and weighing is necessary. Many samples of oleum are solid at ordinary

[1] *Z. anorg. Chem.*, 1916, **98**, 128.

temperatures and must first be liquefied by gentle heating. Care should be taken to avoid the pressure which may be generated in closed vessels during this operation. Products which contain very high percentages of anhydride sometimes do not liquefy completely, a portion remaining as a gelatinous residue. This residue is, however, of the same composition as the liquid portion so that the sample may safely be taken from the latter.

The sampling of solid sulphuric anhydride is difficult. This substance, which is sent out in iron containers as a regular article of trade, is much too compact and tough to enable a sample to be taken out by means of an auger. Before using it, the iron vessels are always heated till the anhydride has completely liquefied; but in this state the oleum emits such a dense cloud of fumes that any sampling is out of the question. The way out of the difficulty is this: In a stoppered bottle some lumps of the solid anhydride are weighed off on a large balance and are then mixed with a sufficient quantity of accurately analysed 100 per cent. sulphuric acid, to form an acid of 70 per cent. of free trioxide, which is liquid at ordinary temperatures. The solution is promoted by gently heating the bottles, say to 30° or 40°, with the stopper loosely inserted. At last a sample is taken out and the analysis performed in the usual way, taking account of the slight proportion of water present in the "monohydrate" employed.

(i) *The Estimation of Total Acidity.*—The great variety of methods of effecting this simple operation is due mainly to two reasons. It is difficult to weigh out small quantities of oleum, particularly if it is very concentrated, without loss by fuming, or to add excess of water without the same trouble. It is more important than usual to avoid such losses on account of the unusual precision which is required of the estimation. The quantity sought is always the free trioxide. Oleum of 20 per cent., for instance, ranks as sulphuric acid of 104·5 per cent. H_2SO_4, so that an error of 0·21 per cent. in the estimation gives a result for the free trioxide, which is wrong by 1 per cent. In this case the whole of the free trioxide corresponds only to 4·5 per cent. of the 104·5 actually estimated, and even the pure trioxide corresponds only to 22·5 per cent. out of 122·5.

The acidimetric titration nevertheless remains the standard, to which all others are referred. Normal sodium hydrate solution is generally used, with either methyl orange or methyl red as indicator. The latter is coming more generally into use for this purpose on account of its sharper end-point and clearness in indifferent light.

The sample is weighed either in glass bulbs or in a glass tap-tube. The method given in Lunge's *Technical Chemists' Handbook* may be given first.

The glass tubes (first proposed by Clas and Gaier in 1881) are very thin bulbs of about ¾ in. diameter, ending each way in a capillary tube. The liquefied acid (2 or 3 gm.) is sucked into the bulb, without danger to the operator, by means of a bottle closed with an india-rubber cork, through which passes a tightly-fitting glass tap, connected at its free end with a rubber tube. Suction is applied to the latter, the tap is closed, the rubber tube is drawn over one of the capillary ends of the weighing-bulb, and by opening the tap a sufficient quantity of acid is admitted into the bulb.

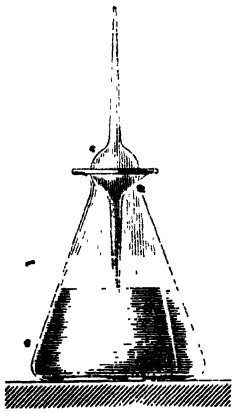
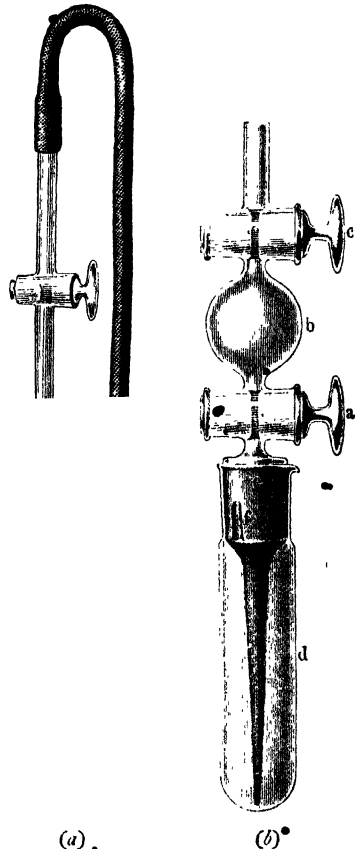


FIG. 6.

The capillary tube is cleaned and one of the two ends is sealed at the lamp. The other end can be left open without fear of any loss or absorption of moisture during weighing. The weighing is best done on a small platinum crucible with two notches, on which the ends of the bulb can rest. If the bulb should be accidentally broken, the acid runs into the crucible, not on to the balance. Then the bulb, open end downwards, is put into a small Erlenmeyer flask, into the neck of which it should fit exactly (Fig. 6), and which contains so much water that the capillary tube dips into it far enough to prevent any loss on mixing the acid with water. Now break off the other point, allow the acid to run out, squirt a few drops of water into the upper capillary, and ultimately rinse the whole bulb-tube by repeated aspiration of water. Dilute the liquid to 500 c.c. and take 50 c.c. for each test. The titration is performed with fifth-normal soda.

In place of the bulb-tube the glass tap-tube shown in Fig. 7(*a*) is often preferred. The tap should be tight without grease, and the tube should taper gradually. It is charged by suction, preferably with only sufficient acid for direct titration without aliquot division. The tap is then closed, and the tube is cleaned and weighed at once. The contents are discharged by allowing them to flow into water in which the point is immersed, or in the case of very concentrated oleum, into a layer of coarsely powdered Glauber's salt. The tube is then cautiously rinsed out with water. Anhydride once melted and drawn into the tube remains liquid long enough for these operations to be completed.



(*a*) (*b*)

FIG. 7.

A useful apparatus for weighing fuming sulphuric acid (as well as other fuming-acids or substances evolving vapours) is the "bulb-tap pipette," constructed by Lunge and Rey,[1] and shown in Fig. 7(*b*). The filling, weighing, and discharging are performed without any loss of vapour and without any special aspirating apparatus. Above the tap *a* there is a bulb *b*, rather less than an inch in diameter, and above this a second tap *c*. The lower portion of the pipette is ground into a glass tube *d*, closed at the bottom. In the conical, ground part of the pipette there is a groove *e*, reaching half-way down, the corresponding half of the groove *f* being in the outer tube. By turning the pipette the tube *d* can be made to

[1] *Z. angew. Chem.*, 1891, 165.

communicate with the outer air, or can be shut off from it altogether. When the pipette is to be used, tap *a* is closed and some of the air is sucked out of *b*, the tap *c* being closed with the suction on. The point is then dipped into the acid to be tested, tap *a* is cautiously opened and is shut when sufficient acid has been drawn in. The pipette is cleaned outside, put back into *d*, and weighed. In most ordinary cases (with other acids, ammonia, etc.) the grooves *e* and *f* are made to communicate; water is squirted through *c* into *b* and then run through *a*, with the contents of the pipette, into *d*, the air escaping through *e* and *f*. The dilute acid is run into a beaker and titrated. In the case of oleum it is preferable to take the pipette out of *d*, rinse the latter into a beaker, run the contents of the pipette, by opening *a*, into water or

FIG. 8.

Glauber's salt contained in the same beaker, then squirt water through *c* (during which time *a* may be closed), and rinse the pipette into the same beaker.

Brewster[1] recommends running the sample, taken by a Lunge pipette, by means of a small glass tube bent at a right angle at the bottom, into a small Erlenmeyer flask, containing 15 c.c. water, and washing the tube with a little water. The results are said to be concordant up to 0·05 per cent.

A very satisfactory and widely used method is that first described as in use at Freiberg.[2] Small glass bulbs of about the dimensions shown in Fig. 8 are made in the blow-pipe, weighed, and are then filled by dipping one of the fine capillary ends into the acid, suction being applied at the other by means of a fine rubber tube. Sufficient oleum is drawn into each to neutralise from 30 to 40 c.c. of normal soda. The bulbs are cleaned on the outside and placed in readiness for weighing on

[1] *J. Amer. Chem. Soc.*, 1907, **29**, 1376.
[2] Rosenlecher, *Z. anal. Chem.*, 1898, **37**, 209.

a wooden or cardboard stand with the points upwards. Care must be taken that the bulb is about three-quarters full, or it may not sink in the titration liquid. No loss or attraction of moisture need be feared during weighing, but the bulbs must not be touched with the fingers. Each bulb is weighed with a small crucible as support, the ends pointing upwards, and is then dropped into a half-litre, stoppered, wide-mouthed bottle containing about 100 c.c. of distilled water. The stopper is inserted immediately and tightly. The bulb may often be broken by hitting a sharp blow on the table with the bottom edge of the bottle. Sufficient time is allowed for all fume to dissolve and the stopper is then removed and rinsed into the bottle, after which the bulb and capillaries are crushed with a stout glass rod. The rod and the sides of the bottle are rinsed down with water and the greater part of the $N/1$ soda required is run in. Indicator is then added and the titration finished. This method is rapid and accurate. It is in use in many laboratories, and was the standard procedure in all H.M. Factories during the War.

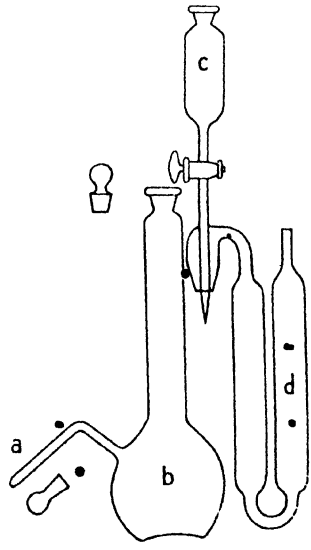


FIG. 9.—Apparatus for Finch's Method of Trioxide Determination.

When great accuracy is required, as for the standardisation of one of the more empirical methods given below, the procedure described by Finch[1] may be adopted with advantage. The apparatus employed is shown in Fig. 9. The flask *b* with its two stoppers are dried and weighed, and 20 to 30 gm. of the sample to be analysed is drawn by suction into the flask through the small side tube *a*. Both stoppers are put in place and the flask again weighed. The second half of the apparatus is prepared for use by filling the funnel *c* with water, and by pouring into the side tube *d* sufficient water to half fill it. By blowing at the open end of *d* the water is driven just up to the

[1] *Z. ges. Schiess- u. Sprengstoffw.*, 1910, 75, 167.

narrow part of the other limb, and is maintained there by keeping one finger on the open end. The stopper of the flask is then quickly withdrawn and the flask and U-tube are fitted together. To decompose the oleum, water is dropped into the flask from *c* with the greatest caution. Every addition of a drop causes an expansion of the gas in the flask, but the water remains near the top of the inner limb of the U-tube, and would have to be driven past the bottom before anything escaped. Cooling of the flask is of course necessary. When the requisite quantity of water has been added, the acid is washed out of the flask and U-tube, and made up to a definite volume for titration or other analysis.

Vernon[1] found that the first energetic reaction sometimes drove the water entirely out of the side tube, and to obviate this described a modification of Finch's apparatus.

The methods of sampling and analysis employed by Messel are given in detail by Gaunt, Thomas, and Bloxam.[2]

Whatever acidimetric method is used, care must be taken that the estimation of sulphuric acid is not vitiated by the presence of any other acid. Nitrous acid may occasionally be present but sulphur dioxide is most common, and although the percentage is frequently very small, the fact should be established that this percentage is insufficient to affect the results, for, as has already been pointed out, an error of 1 in 100 in estimating the sulphuric acid involves an error five times as great in the amount of free anhydride. The estimation of the sulphur dioxide offers no serious difficulty. Oleum of moderate strength can be run into water and the sulphurous acid determined by titration with iodine, or by any other appropriate method which is also applicable to the analysis of ordinary sulphuric acid.

The results of the titrations are calculated to percentages of total SO_3 present, the acidity due to sulphur dioxide being subtracted if necessary, and the free trioxide is then calculated as $S - 4{\cdot}444(100 - S)$, S being the percentage of total SO_3. This calculation can be dispensed with by using the following table:—

[1] *Chem. Zeit.*, 1910, **34**, 792.
[2] *J. Soc. Chem. Ind.*, 1907, **26**, 1175.

Percentages of Free and Total Trioxide in Oleum.

SO_3.		SO_3.		SO_3.		SO_3.		SO_3.		SO_3.	
Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.	Total.	Free.
81·63	0·0	84·7	16·7	87·8	33·6	90·9	50·5	94·0	67·3	97·0	83·7
81·7	0·4	84·8	17·2	87·9	34·1	91·0	51·0	94·1	67·9	97·1	84·2
81·8	0·9	84·9	17·8	88·0	34·7	91·1	51·6	94·2	68·4	97·2	84·8
81·9	1·5	85·0	18·3	88·1	35·2	91·2	52·1	94·3	69·0	97·3	85·3
82·0	2·0	85·1	18·9	88·2	35·8	91·3	52·6	94·4	69·5	97·4	85·8
82·1	2·6	85·2	19·4	88·3	36·3	91·4	53·2	94·5	70·1	97·5	86·4
82·2	3·1	85·3	20·0	88·4	36·8	91·5	53·7	94·6	70·6	97·6	86·9
82·3	3·6	85·4	20·5	88·5	37·4	91·6	54·3	94·7	71·2	97·7	87·5
82·4	4·2	85·5	21·0	88·6	37·9	91·7	54·8	94·8	71·7	97·8	88·0
82·5	4·7	85·6	21·6	88·7	38·5	91·8	55·4	94·9	72·2	97·9	88·6
82·6	5·3	85·7	22·2	88·8	39·0	91·9	55·9	95·0	72·8	98·0	89·1
82·7	5·8	85·8	22·7	88·9	39·6	92·0	56·4	95·1	73·3	98·1	89·7
82·8	6·4	85·9	23·2	89·0	40·1	92·1	57·0	95·2	73·9	98·2	90·2
82·9	6·9	86·0	23·8	89·1	40·6	92·2	57·5	95·3	74·4	98·3	90·7
83·0	7·5	86·1	24·3	89·2	41·2	92·3	58·1	95·4	75·0	98·4	91·3
83·1	8·0	86·2	24·9	89·3	41·7	92·4	58·6	95·5	75·5	98·5	91·8
83·2	8·5	86·3	25·4	89·4	42·3	92·5	59·2	95·6	76·1	98·6	92·4
83·3	9·1	86·4	26·0	89·5	42·8	92·6	59·7	95·7	76·6	98·7	92·9
83·4	9·6	86·5	26·5	89·6	43·4	92·7	60·3	95·8	77·1	98·8	93·5
83·5	10·2	86·6	27·0	89·7	43·9	92·8	60·8	95·9	77·7	98·9	94·0
83·6	10·7	86·7	27·6	89·8	44·5	92·9	61·3	96·0	78·3	99·0	94·6
83·7	11·3	86·8	28·1	89·9	45·0	93·0	61·9	96·1	78·8	99·1	95·1
83·8	11·8	86·9	28·7	90·0	45·6	93·1	62·4	96·2	79·3	99·2	95·6
83·9	12·3	87·0	29·2	90·1	46·1	93·2	63·0	96·3	79·9	99·3	96·2
84·0	12·9	87·1	29·8	90·2	46·6	93·3	63·5	96·4	80·4	99·4	96·7
84·1	13·4	87·2	30·3	90·3	47·2	93·4	64·1	96·5	81·0	99·5	97·3
84·2	14·0	87·3	30·9	90·4	47·7	93·5	64·6	96·6	81·5	99·6	97·8
84·3	14·5	87·4	31·4	90·5	48·3	93·6	65·2	96·7	82·0	99·7	98·4
84·4	15·1	87·5	31·9	90·6	48·8	93·7	65·7	96·8	82·6	99·8	98·9
84·5	15·6	87·6	32·5	90·7	49·4	93·8	66·2	96·9	83·1	99·9	99·5
84·6	16·2	87·7	33·0	90·8	49·9	93·9	66·8	...	...	...	...

(ii) *The Direct Estimation of Free Anhydride.*—The free anhydride in oleum may be estimated very quickly by measuring the heat given out when sufficient water is added to hydrate it completely. To add pure water for this purpose is inadvisable, and to pass the oleum into water is to involve the production of a large proportion of the heat by the sulphuric acid present, as distinct from the free anhydride. Howard obviated this difficulty by mixing the acid with sulphuric acid of 92 per cent.[1] A suitable volume of the 92 per cent. acid is run into a silvered vacuum vessel. A Thermos flask does very

[1] *J. Soc. Chem. Ind.*, 1910, 29, 3.

well, or a cordite heat-test vessel. The temperature of this acid is taken, and an equal volume of oleum, the temperature of which is taken at the same time, is then poured in. The liquid is well mixed and the temperature noted which the mixture attains. Suppose t_a, t_o, t_m are the observed temperatures of acid, oleum, and the mixture, the increase of temperature is calculated as $I = t_m - (t_a + t_o)/2$. The tests should be carried out with a range of oleum samples which have been carefully analysed by the usual methods, and a curve of calibration constructed for the particular vessel, strength of acid employed, and other conditions of experiment. Once this calibration has been carried out, the method proves to be a very reliable and rapid one. It is surprisingly sensitive to small changes in free anhydride content, and is, in fact, a more certain indication of these, as between one sample and another, than is the acidimetric method, unless performed with extreme care. It works well for all oleum up to 30 per cent., but is not very convenient for stronger material without some modification of the procedure. Variations in the strength of the acid, say from 83 to 91 or 92, have hardly any effect. Howard showed that by using the method the other way round, *i.e.*, by pouring first into the flask a known volume of oleum of say 20 per cent., and then adding sulphuric acid of any concentration under 100 per cent., it could be employed as a very rapid test for the latter. In this case, of course, free trioxide must be in excess throughout the experiment.

Howard's method has been modified in detail with a view to providing a simple test which can be entrusted to workmen in the operation of plant.[1] The simplest possible apparatus is required—an earthenware mug or jar holding about a pint, two glass cylinders holding each 200 c.c., and a thermometer, which is preferably protected by sealing into a light iron case perforated with holes at the lower end. To carry out the test, measure 200 c.c. of sulphuric acid (92·5 to 94·5 per cent.) into the mug and have ready 200 c.c. of oleum in the cylinder. Take the temperature of each, and then quickly pour the oleum into the acid, stirring vigorously all the time. Note the

[1] Curtis and Miles, *J. Soc. Chem. Ind.* (*Trans.*), 1920, 39, 64.

maximum temperature of the mixture and reckon the increase $I = t_m - (t_a + t_o)/2$ as above. Reference to the table below gives the percentage of free anhydride:—

Plant Test for Free Trioxide in Oleum.

Increase of temp. *I*.	Per cent. SO_3.	Increase of temp. *I*.	Per cent. SO_3.	Increase of temp. *I*.	Per cent. SO_3.	Increase of temp *I*	Per cent SO_3.
1	...	11	5·9	21	12·1	31	18·7
2	0·0	12	6·5	22	12·8	32	19·4
3	0·6	13	7·2	23	13·4	33	20·1
4	1·3	14	7·8	24	14·1	34	20·8
5	2·0	15	8·5	25	14·7	35	21·4
6	2·6	16	9·7	26	15·4	36	22·0
7	3·2	17	9·1	27	16·0	37	22·7
8	3·9	18	10·3	28	16·7	38	23·4
9	4·6	19	10·9	29	17·4	39	24·1
10	5·3	20	11·5	30	18·0	40	24·7

The results from this table are correct to within ±0·5 per cent. of free anhydride. For ordinary clear oleum the relation: Percentage of free trioxide = 0·658 $(I-2)$ is very nearly correct. The strength of the diluting acid may vary from 92·5 to 94·5 without any appreciable difference resulting. It is nevertheless advisable to use the same acid consistently. The samples of oleum should be cooled, at least to 25°. It has been observed that in one case caution in using the method is necessary. The rise in temperature observed with oleum made from sulphuric acid recovered from the waste acid from T.N.T. nitration is always greater than with a clear oleum, or an oleum made from acid recovered from nitro-glycerine manufacture.

In practice the "Heat Rise" test as described in the foregoing has proved to be accurate and more rapid than any other test not requiring complicated apparatus. It may also be carried out in the inverse manner as a test for the acidity of ordinary acid, and as this rapid estimation is a desideratum in oleum plant work, as well as the estimation of oleum, the necessary data may be usefully quoted. In the case of sulphuric acid of 96 to 100 per cent. H_2SO_4 proceed exactly as before, with the exception that the acid must be poured *into* the oleum, which should be of not less than 20

per cent. strength. After mixing, the liquid should fume. (See p. 70.)

In the case of sulphuric acid containing from 88 to 96 per cent. H_2SO_4, the test is best made by taking 300 c.c. of oleum (temperature t_o) and pouring into it 100 c.c. of the sample of acid (t_a), stirring vigorously. If the maximum temperature is t_m, the increase is reckoned as $I = t_m - (3t_o + t_a)/4$, and the

Plant Test for 96 to 100 per cent. Sulphuric Acid.

Increase of temp. *I.*	Per cent. H_2SO_4.	Increase of temp. *I.*	Per cent. H_2SO_4.	Increase of temp. *I.*	Per cent. H_2SO_4.
2	99·9	12	98·4	22	96·9
4	99·5	14	98·1	24	96·3
6	99·3	16	97·8	26	96·4
8	99·0	18	97·5	28	96·1
10	98·7	20	97·3	30	95·8

percentage is ascertained from a table similar to those given, and constructed from a graph drawn to represent the results of a number of estimations in the range required.

Another method, which has been fully developed for estimating free anhydride directly, consists in determining the water necessary to reduce the oleum to 100 per cent. sulphuric acid. According to Setlik,[1] 50 or 100 gm. are weighed out in a long-necked flask, and water is dropped in very slowly from a burette till the fuming has ceased. During the operation the flask must be well cooled. In order to observe the end-point, the flask must be agitated after adding each drop of water until the fumes have been entirely absorbed by the acid. When no fumes whatever are formed at the surface and a drop falling into the middle of the acid dissolves quietly, the end-point is reached. Acid of more than 35 per cent. must be previously diluted with monohydrated sulphuric acid. Setlik claimed that this plan is much more expeditious and quite as exact as the alkalimetrical way; but the analytical proofs adduced do not bear this out, for there are deviations up to 0·9 per cent. of free trioxide.

[1] *Chem. Zeit.*, 1889, **13**, 1670.

A more recent examination of this method has been made,[1] from which it appears that duplicate titrations agree very closely with each other, and that the results compare closely with those obtained alkalimetrically. The procedure recommended for an acid containing 20 to 40 per cent. of anhydride is the following. From 50 to 75 gm. of the sample are weighed into a 50 c.c. stoppered cylinder of thin glass, or a large stoppered test-tube. Distilled water is then run in slowly from a burette, with frequent vigorous shaking, so that the white fumes which form after the addition of water are completely absorbed. From time to time air is blown through a glass tube across the surface of the acid, fumes being formed so long as any free anhydride remains. The fuming decreases towards the end of the titration and suddenly stops. The operation must be carried out in a good light and the temperature of the acid must be kept below 40°, for about this temperature 100 per cent. sulphuric acid begins to fume, although it does not fume at the ordinary temperature. In experiments in which the temperature was allowed to rise to 90° and then fall to 80°, the anhydride indicated by the test was about 2·0 higher than usual, *i.e.*, 34 per cent. instead of 32 per cent.

It is of course possible to replace the water by sulphuric acid of known water content. Although the alteration is a convenient one and the rise of temperature is less serious, the disadvantage of working with a titrating liquid liable to change and not in any case of standard composition, more than outweighs the gain.

The electric conductivity can also be used as a measure of the sulphur trioxide concentration, and methods have been developed in some works. It is extremely rapid and can be applied to a slow continuous stream of either oleum or sulphuric acid, by suitable means. The apparatus may consist in essentials of a simple form of Kohlrausch bridge with appropriate resistances, telephone, and induction coil, connected to the conductivity cell in the usual way. The sample is poured into, or run continuously through the cell, or some simple form of immersion electrode may be dipped into the sample bottle, and a reading obtained on the slide-wire of

[1] Parker, *J. Soc. Chem. Ind.* (*Trans.*), 1917, 88, 693.

the bridge. This gives the required percentage at once, if a previous calibration of the bridge has been made with analysed samples. It is necessary in using this method to know in what region the results are expected to lie, or confusion may arise from the possibility that two samples of oleum of different concentrations (or three of sulphuric acid) may have the same conductivity.

The Estimation of Arsenic in Oleum and Sulphuric Acid.—It is of the greatest importance in connection with the Contact Process to be able to determine regularly the small amounts of arsenic, not only in the oleum made, but also in the various acids used in the stages of purification and absorption. Two standard methods of doing this are available—the Marsh and the Gutzeit tests. In either case the difficulties connected with the purification of zinc should be avoided and the electrolytic method used, preferably in the form devised by Sand and Hackford.[1] The apparatus is shown in Fig. 10. A is an external cooling vessel, B the anode compartment, and D the cathode compartment—a glass tube of 1⅝-inch bore and 7 inches long, closed at the upper end by a rubber stopper and at the lower by a disc of parchment paper tied while wet over the rim of the tube with string. The leaden anode C is lid-shaped at the upper end in order to minimise the spraying, and in the cylindrical part which fits round the cathode tube a vertical slot 5 inches high is cut (S), so that the cathode may be observed. The bottom edge is bent inwards to form a rim on which the cathode tube (preferably supported on a glass triangle to give room for escaping oxygen) may rest. Through the rubber stopper passes a funnel F and the cathode E. This is made of pure lead, and the lower end, which should almost touch the parchment diaphragm, is 1 inch high by ¾ inch wide. In the drying tube G are placed (*a*) lead acetate paper, then calcium chloride, and (*c*) cotton wool. The hard glass tube required for the Marsh test is attached to the drying tube with a rubber stopper.

To carry out a test 100 c.c. of a solution containing a little ferrous sulphate and stannous chloride and about 1 gram of the acid is poured into the cathode tube, the outer compart-

[1] *J. Chem. Soc. Trans.*, 1904, 85, 1018.

ment having been filled with arsenic-free sulphuric acid of 10 per cent. concentration. A current of 5 to 6 amps. is maintained through the cell for thirty to forty-five minutes, the temperature being kept down to 15° to 20° by running cooling water through the outer jacket. The arsenic mirror is obtained and evaluated in the usual way, due attention being paid to blank tests.

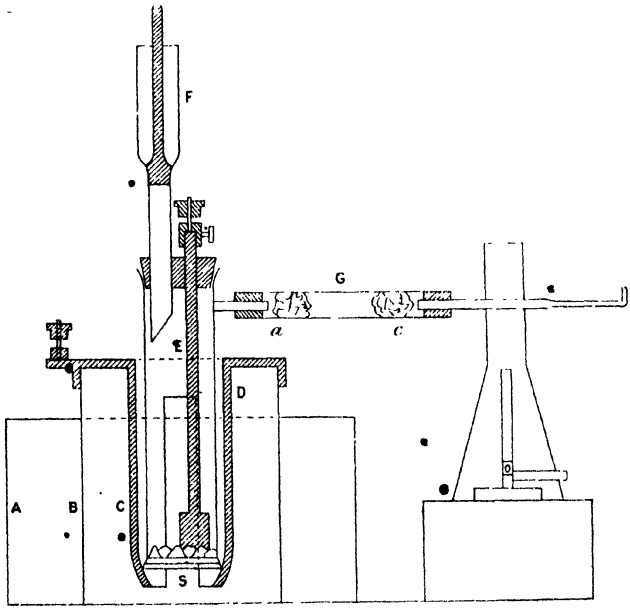


FIG. 10.—Apparatus for Electrolytic Marsh or Gutzeit Test.

Sand and Hackford stated that with this apparatus 0·0005 gram of arsenic could be detected with certainty in 50 c.c. of liquid.

Instead of the Marsh procedure that of the Gutzeit test can be adopted, with a gain in convenience, for commercial sulphuric acids. The hard glass tube and burner are then replaced by a slip of filter paper impregnated with mercuric chloride or bromide, through which the gas is made to pass. Many modifications of this have been described, many of them having in view the adjustment of the impregnated paper. In

one which can be recommended, that of Hibbert,[1] the drying tube (which would replace G in Fig. 10) is made vertical and a simple spring clamp is used to secure a *strip* of paper between the upper ground end of the tube and a celluloid or vulcanite washer perforated with a 5-mm. hole. In case the arsenic found exceeds the usual amount, the strip can be moved along when necessary during a test, exposing fresh paper each time. Another simple device—a rubber stopper half cut through—has also been noted.[2]

[1] *J. Soc. Chem. Ind.*, 1916, **35**, 672.
[2] *Analyst*, 1919, **44**, 235.

CHAPTER III

GAS-REPEAT EQUILIBRIUM AND VELOCITY OF REACTION

THE reaction between sulphur dioxide and oxygen possesses not only vast technical importance but also great intrinsic interest. It has been investigated from many sides. Numerous series of experiments have been made to define the conditions under which the reaction will give good results in practice, and to evaluate the obtainable yields. From the scientific point of view also, the phenomena of catalysis at solid surfaces has always been a problem of the most vivid interest to chemists. The results of all this work, carried out with the principles of the Law of Mass Action always in view, present a mass of experience, both practical and theoretical, which is—even with many outstanding unsolved problems—one of the greatest achievements of chemistry.

At the ordinary temperature and at any pressure so far employed, sulphur dioxide and oxygen are entirely without action on one another. Nor does increase of temperature alone appear to produce any direct action; some slight combination does certainly take place, but there is overwhelming evidence for believing that this is due in every case to the action of the surface of the inevitable containing vessel. It is true, also, that sulphur in burning gives some trioxide, but that this is formed from the dioxide and apart from solid surfaces, has never been shown. In general, to cause combination it is necessary to submit the mixture of gases to other forces. The passage of electric sparks or the silent electric discharge, for instance, cause formation of trioxide. Ultra-violet light acts in the same way.

The whole of the technical possibilities of the direct combination of these two gases lies in the influence which is exerted on them by certain solid substances. These substances

—known as catalysts—have the power of causing combination to occur and retain at the end of the catalytic change the same chemical, if not physical, individuality they had at the beginning. Any solid substance which does not set up other chemical changes and so become converted into something else, seems to be capable in this case of exerting this *catalytic* influence in a greater or a less degree. Metallic oxides, silica, carbon, porcelain, kieselguhr, and many metals are all more or less efficient. Platinum has been found to act with a rapidity unsurpassed by that of any other substance. It is alone capable of exerting an influence sufficient to secure reasonably rapid combination at temperatures which must not exceed 450° by many degrees. Many other catalysts have been proposed for the reaction. Their properties and behaviour will be discussed later. Some of them possess sufficient activity at temperatures higher than 450°, but the use of such high temperatures defeats the end in view. Platinum has no serious rival.

Investigation of the phenomena of catalysis in systems of gases containing a solid phase has shown that the effect is largely a surface one. Although the mechanism of the process has to some extent been discovered, the actual cause and origin of the catalysis is not known to us.

The available facts regarding this surface action will be discussed later; for the present it is sufficient to define a catalyst in the well-known terms as a substance which, without appearing among the products of a reaction, alters its velocity. Objection may be made to this statement in the present instance, on the ground that, in the absence of a catalyst, the reaction has no velocity to alter; but this may be met, although perhaps in a rather artificial way, by admitting that the reaction does actually proceed, though with a velocity which is immeasurably small.

A reaction between gases, however, does not usually go on until all the substances initially present have been used up, even although these were present, to begin with in the required molecular proportions. Frequently a point is reached beyond which combination cannot go, some of the original materials being still uncombined. An equilibrium is set up, at which, if the original reaction of combination be imagined to be still

in progress—as the kinetic conception of gases would imply—it must be balanced by the opposing reaction between the substances resulting from the first reaction, proceeding exactly at the same rate. The reaction we are dealing with is one of these, and the state of affairs mentioned has to be taken into practical account, for at temperatures which may be the lowest that can be maintained in practice, the point of equilibrium may be so unfavourably situated that a high yield of trioxide cannot be obtained. This is particularly likely to be the case when inactive catalysts are in use.

The catalytic substances that may be selected vary greatly in composition and properties, but in every case—at a given temperature—the same equilibrium[1] is reached. That is, starting always from the same mixture of sulphur dioxide and oxygen, the amount of combination will be the same, no matter what the catalyst. A moment's reflection on the action of two catalysts at once in the same gas mixture, will show the impossibility of the same equilibrium *not* being reached, and in addition there is, in connection with this particular reaction, considerable experimental proof.

If this is borne in mind, and the condition of equilibrium is viewed as the balance of two opposing reactions, it follows that the influence exerted by the catalyst on the velocity of each reaction must be of the same order. Experiment is in accord with this. We should expect that any catalyst which would enable the two gases initially to combine, would have a corresponding tendency to dissociate the resulting compound into its components. Knietsch showed that this actually occurred. The combination of sulphur dioxide and oxygen at the surface of porous porcelain was of the same rapidity as the decomposition of sulphur trioxide under the same conditions. Platinum, which effects incomparably more rapid conversion, resolved the compound correspondingly faster. In the words used by Ostwald, the catalysis of a reaction may be recognised by the fact—a very evident and fundamental one for the present example—"that on account of the addition of a

[1] Equilibrium in the gas removed from the immediate neighbourhood of the catalyst. There is some evidence that if the proportionate amount of catalyst is very high, the equilibrium in the gas as a whole may not follow this rule.

catalysing material, the velocity with which a given reaction attains its state of equilibrium is more or less increased."

This is all that the catalyst can do. The particular equilibrium arrived at is determined, and the proportion of conversion of sulphur dioxide to trioxide is fixed, by conditions of temperature, pressure, and original concentration of the reacting substances. All these are quite independent of the catalyst. An active catalyst causes equilibrium to be reached very rapidly, a feeble one may require more than reasonable time, but in either case the maximum yield is that obtained at the equilibrium point. Hence it is of the greatest importance to have accurate knowledge of the equilibrium at various temperatures. Experimental work has been done with this in view, and will be described in a later section. The most active catalyst, platinum, is always used for such work to make certain that equilibrium is actually reached; but the results depend only on the thermal properties of the gases themselves, so that the catalyst may therefore, for the present at least, be omitted from the discussion.

The Gas Equilibrium.

The statement that equilibrium is attained by balanced opposing reactions may be expressed symbolically:—

$$2SO_2 + O_2 \rightleftharpoons 2SO_3.$$

The reaction from left to right gives out heat. Suppose now that a mixture of all three gases in equilibrium is raised in temperature. In accordance with the Principle of Movable Equilibrium, the system will adjust itself in such a way as to tend to neutralise the imposed change. In this case the tendency will be to absorb heat, which can occur only by sulphur trioxide dissociating. Increase of temperature has thus established a new state of equilibrium, in which the yield of trioxide is less than before. From this elementary reasoning the fundamental problem of the contact reaction appears at once. The higher the temperature the worse is the yield. Good yields are therefore attainable in proportion to the activity of the catalyst, for the more active the catalyst, the lower its working temperature.

The effect of increasing the pressure may be predicted in

the same way. Reaction in the direction of combination results in a smaller volume. Application of pressure to the whole system will therefore lead to the system tending to occupy less volume, *i.e.*, more combination will occur. Increased pressure, therefore, helps the end in view, but the practical importance of pressure is small. In other reactions, such as the synthesis of ammonia, it may be of paramount importance. Attempts have been made to conduct the Contact Process under increased pressure, and patent specifications still view the possibility of doing so; but, as will be seen later, the maximum possible gain is not sufficient to make such a technical elaboration worth while.

As regards the proportion of sulphur dioxide and oxygen with which the reaction is begun, it is clear that according to the Principle of Mass Action, the more oxygen we have present originally, the greater will be the chance of forming trioxide. Excess of oxygen beyond that actually required for combination will therefore be an advantage.

It remains now to obtain a quantitative and detailed expression for what has been discussed qualitatively and generally. If we express the proportions of oxygen, sulphur dioxide, and trioxide in the form of partial pressures, and if p_{O_2}, p_{SO_2}, p_{SO_3} are these partial pressures *at equilibrium*, we have at a given temperature, according to the quantitative form of the Mass Action law:

$$K_p = \frac{p^2_{SO_2} \cdot p_{O_2}}{p^2_{SO_3}}$$

K_p being a constant at the particular temperature considered. Instead of partial pressures (in atmospheres) concentrations (in gram-molecules to the litre) are often used. Denoting these by C_{O_2}, etc., the equation becomes:—

$$K_c = \frac{C^2_{SO_2} \cdot C_{O_2}}{C^2_{SO_3}} \quad . \quad . \quad . \quad (2).$$

The form generally given in the literature involves K_c as in (2), but for practical purposes percentages by volume are generally used, and these are more readily converted to partial pressures than to concentrations, so that partial pressures will be adhered to in this section for purposes of calculation.

Another change also is desirable, for the constants K_c and K_p have very inconvenient values which are not easily remembered. K_c at 400°, for instance, is $7{\cdot}81 \times 10^{-8}$ K_p is $4{\cdot}32 \times 10^{-6}$, and at 600° K_c is $1{\cdot}3 \times 10^{-4}$. In view of this it is convenient to adopt the form proposed by Haber:—

$$k_p = \frac{p_{SO_3}}{p_{SO_2}} \cdot \frac{1}{\sqrt{p_{O_2}}} \quad . \quad . \quad . \quad (3).$$

In this k_p is greater than unity for all but very high temperatures, and in addition, its value is the higher, the more favourable the equilibrium to trioxide formation. Even at the lowest temperatures that can be used, k_p does not exceed the hundreds numerically. The connection between the three functions is a simple one, for instead of the usual form of the equation of state

$$pv = RT$$

we may write

$$\frac{p}{C} = RT$$

in which p is measured in atmospheres and C is the number of gram molecules in 1 litre; T is the absolute temperature, and the value of R for these units is 0·0821. From this and the three equations given

$$k_p = \frac{1}{\sqrt{K_p}} = \frac{1}{\sqrt{0{\cdot}0821\,T}} \frac{C^2_{SO}\,C_{O_2}}{C^2_{SO_3}} = \frac{1}{\sqrt{0{\cdot}0821\,TK_c}} \quad . \quad . \quad . \quad (4).$$

At every temperature k_p will have an individual value, and to determine the relation between $T°$ and k_p several series of measurements have been made, of which the most satisfactory are those of Bodenstein and Pohl. They will be discussed in a later section together with the method of utilising them. Curve v. of Fig. 11 has been plotted from these data. It is once apparent that k_p decreases very rapidly as the temperature rises, and since from (3) a low value of k_p implies a low ratio of trioxide to dioxide, temperature is seen at once to be the factor on which yield is most dependent. The equilibrium partial pressure of oxygen (p_{O_2}) has also a certain influence, and it

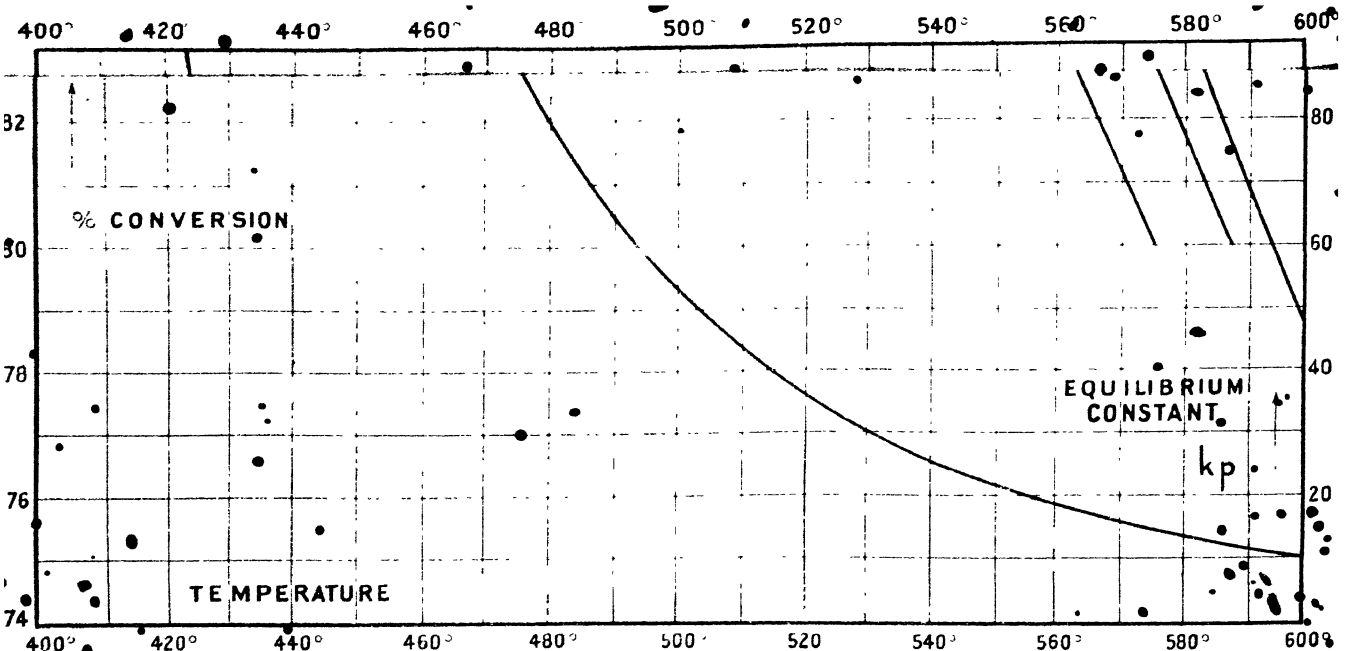


FIG. 11.—Relation between Equilibrium Yield and Temperature for four Gas Mixtures. Curve i—5 per cent. SO_2, 15.9 per cent. O_2 Curve ii—7 per cent. SO_2, 13.9 per cent. O_2; Curve iii—7 per cent. SO_2, 10.4 per cent. O_2; Curve iv—7 per cent. SO_2, 93 per cent. O_2. Curve v—Equilibrium Constant.

[*Face page* 80.

can be seen that from a given mass of dioxide, more trioxide will be formed by increasing p_{O_2} without altering any other factor.

But to obtain these results more clearly and to view generally the most important question of the fractional yield obtainable under equilibrium conditions, it is necessary to transform (3) and write it in terms of the *initial* concentrations of the three gases. Let a be the initial percentage of dioxide by volume, and b that of oxygen. Also let the conversion be expressed as the fraction x. Then when equilibrium is attained $ax/2$ volumes of oxygen have disappeared, and the partial pressures are:—

$$p_{SO_2} = \frac{a(1-x)}{100 - ax/2} \quad p_{SO_3} = \frac{ax}{100 - ax/2}, \; p_{O_2} = \frac{b - ax/2}{100 - ax/2},$$

so that, equation (3) takes the form.

$$\therefore \; k_p = \frac{x}{1-x} \sqrt{\frac{b - ax/2}{100 - ax/2}} \qquad (5).$$

There is no ready means of solving this for x, *i.e.*, we cannot use it to find out what conversion will be obtained for a given temperature and value of k_p, and with a given gas mixture. We can, however, assign various values to a, b, and x, and find what values k_p would represent these conditions, and consequently the temperatures at which they would hold.

The results of some calculations made for this section are set out in the table on page 82.

Three cases have been taken into account: (i) A mixture containing 5 per cent. of dioxide and 15·9 per cent. of oxygen, approximating closely in composition to a 5 per cent. gas mixture in a plant where sulphur is burnt, and such as might be drawn into the converters of a Grillo or similar plant; (ii) a similar mixture containing 7 per cent. of sulphur dioxide instead of 5; and (iii) a mixture containing 7 per cent. of dioxide and only 10·4 per cent. of oxygen—a probable composition for gas drawn from pyrites-burners. The comparison of (ii) and (iii) is interesting on account of the smaller proportion of oxygen which results in case (iii), when pyrites is used instead of sulphur to produce the same concentration of sulphur

dioxide as before. The method of calculation used for finding $t°$, k_p being known, will be discussed in a later section.

The figures are shown graphically in Curves i., ii., and iii. of Fig. 11 in which k_p is also represented. From these curves a clear idea may be gained of the influence of temperature and of the proportion of oxygen on the yield, which under ideal conditions (*i.e.*, with an ample sufficiency of catalyst) is the maximum that can be reached. Temperature is dominant. To

Equilibrium Constants and Yields at Various Temperatures.

Per cent. Conversion.	(i) SO_2, 5 per cent.; O_2, 15·9 per cent.		(ii) SO_2, 7 per cent.; O_2, 13·9 per cent.		(iii) SO_2, 7 per cent.; O_2, 10·4 per cent.	
	$t°$.	k_p.	$t°$.	k_p.	$t°$.	k_p.
99	424	267	...	...	412°	361
98·5	441·5	177	...	...	...	...
98	455·5	132	451	149	...	...
97	475·5	87	470	98	...	...
96	490	64·5	483·5	73	474·5	89
94	512·5	42	506	47	...	...
92	529	31	...	...	512·5	42
90	543	24	537·5	27	526	33
85	572·5	15·1	566	16·8	553	20·4
80	594·5	10·6	588	11·8	575	14·3
75	613·5	7·9	...	...	...	...

obtain 98 per cent. conversion with a 5 per cent. mixture the temperature must not exceed 455°. Maintaining a temperature 50° higher, the maximum yield falls to 94·7. It is in the region between 430° and 460° that the contact action of platinum is usually said to proceed most efficiently. The increasing downward slope of the curve is significant. The further the temperature rises, the more rapidly does the equilibrium diverge from success. If, for instance, the temperature is 520°—a point reached in practice under certain conditions, a further rise of 50° reduces the conversion to about 85·5 per cent.—a fall of 7·6 per cent. instead of about 3·3 per cent. in the former case.

Curve ii. for the 7 per cent. sulphur-burner gas is very similar in form, and indeed lies very close to the first, although

slightly below it. The two curves are almost parallel throughout the region in which they are drawn. Slightly less conversion is to be expected, therefore, from the 7 per cent. mixture, and the difference between the conversions of the two mixtures will be the greater, the higher the temperature and the more unsatisfactory the general result, on account of the increasing downward slope of the curves. Within the usual technical range, the differences in conversion between the two cases are practically very small.

Curve iii. carries the matter further. The oxygen content is diminished to 10·4 per cent. Even in this case, with only two thirds of the oxygen present in the first case, the yield does not fall more than 1 per cent. below that of the first case (5 per cent mixture) until 475° has been exceeded, and not until 505° is reached does the conversion fall 1 per cent. below that in the second case (7 per cent. mixture).

Under technical conditions the enrichment of a gas mixture from 5 to 7 per cent. might conceivably cause overloading of the catalyst and consequent incompleteness of reaction, but it should be emphasised that the addition of more sulphur dioxide to the gas mixture would have no effect on the equilibrium yield at all if the *equilibrium* partial pressure of oxygen remained the same as before. To illustrate this, take the case of mixture (i); the partial pressure of oxygen at equilibrium is p_{O_2}. Suppose the conversion is 95 per cent.—

$$p_{O_2} = \frac{15{\cdot}9 - 0{\cdot}475 \times 5}{100 - 0{\cdot}475 \times 5}.$$

If now the sulphur dioxide is increased to 7 per cent., p_{O_2} becomes—

$$\frac{b - 0{\cdot}475 \times 7}{100 - 0{\cdot}475 \times 7},$$

and if b is made equal to 16·7 (which could be actually done, of course, only by adding oxygen), p_{O_2} has the same value in both cases. A glance at equation (5) shows that so long as p_{O_2} remains unchanged the yield will remain the same.

Curve v. is inserted to show what would be the result of working with pure oxygen instead of air and burning sulphur to produce a 7 per cent. mixture as before. The departure

of this curve from the others is considerable; but even in this impossibly favourable case the gain does not exceed 1·3 per cent. of conversion within the limits 430° to 460°, between which contacts of an efficient type usually work.

It is of some interest to follow the effect of decreasing the oxygen rather further than is shown by Curves i. to iii. This may be done by plotting more similar curves, but the results are more conveniently seen in the curves of Fig. 12 in which, for several temperatures, the initial oxygen percentage is plotted against the percentage yield. The initial percentage of dioxide has been taken throughout as 7. At 440° and 460° the curve is almost a linear one. The oxygen can be reduced to 6 per cent. without more than 2 per cent. of conversion being lost. But below 6 per cent. reduction causes conversion to fall more and more rapidly until 3·5 per cent. is reached. Here at 440°, with the proportion of oxygen demanded by the simple chemical equation, the possible yield is only about 91 per cent. As the temperature rises the reduction of oxygen has an increasingly greater effect. It may therefore be expected that, so far as the equilibrium conditions are concerned, with gas mixtures containing usual amount of dioxide (5 to 8 per cent.) the insufficiency of oxygen will have little result, if the temperatures are favourable, until this gas and the dioxide have equal partial pressures. At temperatures higher than 460° the effect would be more considerable. Considerable variations do certainly occur in practice without any harmful result. The same conclusion can be deduced from the figures of the tables on page 86, which are taken from the paper of Bodenstein and Pohl.

In the foregoing the assumption has been made throughout that the difference between 100 and the combined percentages a and b consisted in every case of nitrogen. This gas does not participate in the reaction, and we should expect its action to be only to dilute the reacting gases—to lower the values of a and b under the root sign in (5), and thus decrease the equilibrium partial pressure of oxygen. Any inert gas would act in the same way. To test this and other conclusions, a series of experiments was made by Knietsch.[1] Mixtures of

[1] *Ber. des Internationalen Kongress für. angew. Chem.*, 1903, 1, 614.

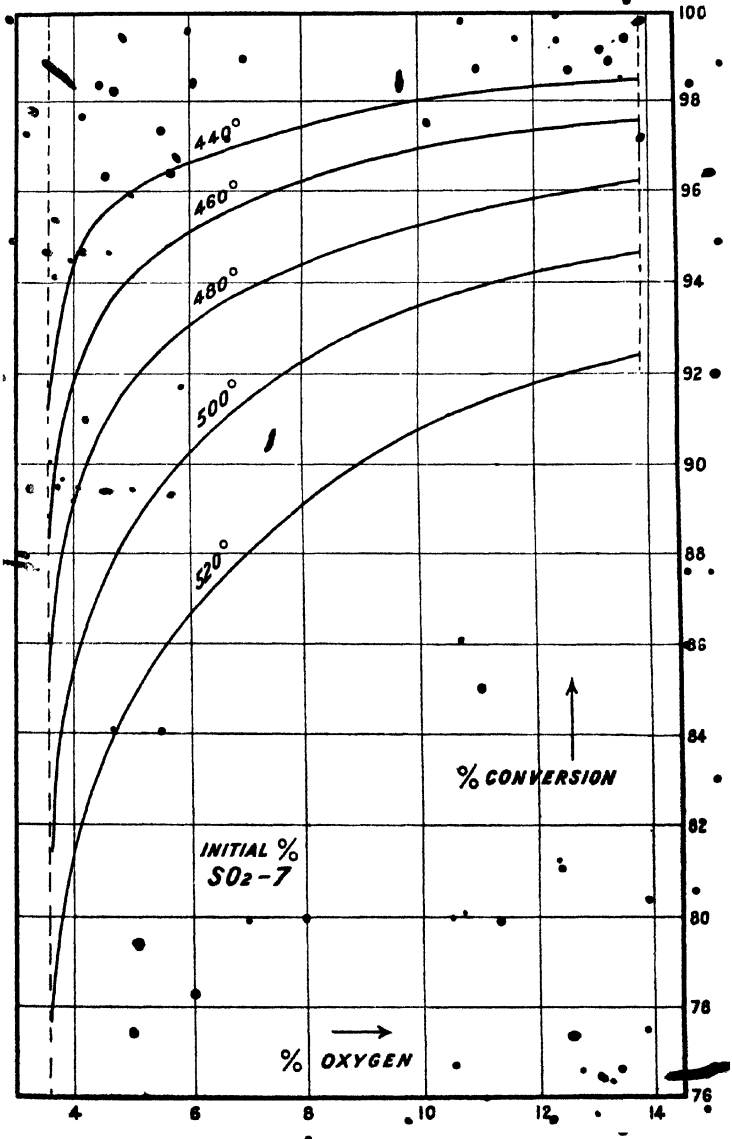


FIG. 12.—Relation between Equilibrium Yield and Initial Oxygen-Percentage for a 7 per cent. Mixture.

Equilibrium Yield of Sulphur Dioxide and Oxygen.

No.	N_2.	SO_2.	O_2.	400°.	500°.	600°.	700°.	800°.	900°.
1	...	66·67	33·33	98·1	91·3	76·3	51·5	30·1	16·9
6	...	33·33	66·67	99·7	97·3	88·5	66·6	40·4	22·0
7	...	14·00	86·00	99·8	97·9	90·3	69·8	43·9	24·4
8	...	7·00	93·00	99·8	98·1	90·5	70·7	44·9	25·3
9	...	2·00	98·00	99·8	98·2	90·8	71·2	45·5	25·6

Equilibrium Yield of Burner-Gas diluted with Air.

No.	Air per cent.	N_2.	SO_2.	O_2.	400°.	500°.	600°.	700°.	800°.	900°.
3	...	84·85	10·10	5·00	96·2	83·2	59·1	31·9	15·0	7·0
10	1·444	83·00	7·00	10·00	99·3	93·4	73·3	42·5	20·5	9·8
11	2·194	81·40	4·00	14·60	99·4	94·9	78·3	48·1	24·2	11·7
12	3·944	80·00	2·00	18·00	99·5	95·6	80·5	51·3	26·3	12·9

various composition containing as diluent, nitrogen, carbon dioxide or water vapour, were passed at a constant rate over platinised asbestos. The experimental method will be referred to later. The experiments were made in pairs so that the diluted mixture and the same mixture without the diluent were passed successively over the catalyst until constant conditions were obtained. All other conditions were carefully held constant. Some of the results are given below:—

No.	Gas Mixture.	Temp. °C.	Before Reaction.			After Reaction.		Conversion per cent. Found.	Conversion per cent. Calculated.
			Per cent. SO_2.	Per cent. O_2.	Per cent. Diluent.	Per cent. O_2.	K_c.		
1*a*.	Stoichiometric mixture	430	66·7	33·3	...	2·84	...	94·0	94·2
„	Stoichiometric mixture + Nitrogen	430	20·0	10·0	70 N_2	1·00	91	90·5	...
1.	Burner-gas	430	7·2	10·4	82·4 N_2	7·15	1134	98·9	...
	Burner-gas + 1 vol. Nitrogen	430	3·6	5·2	91·2 N_2	3·52	...	98·2	98·4
2.	Burner-gas	470	7·2	11·3	81·5 N_2	7·85	84	96·2	...
	Burner-gas + 1 vol. CO_2	470	3·6	5·65	90·75 $\{CO_2, N_2$	3·92	...	94·3	94·7

The two experiments denoted by 1*b* may be instanced. The first of these dealt with burner-gas from an adjacent plant and was carried out with great care. Small, frequent fluctuations occurred, but over a long time the composition of the mixture was said to be very constant. From the analysis of the converted mixture in the first experiment the constant K_f was found by means of the equation :—

$$K_f = \frac{P^2_{SO_3}}{P^2_{SO_2} P_{O_2}}, \quad \text{or} \quad \sqrt{K_f P_{O_2}} = \frac{P_{SO_3}}{P_{SO_2}}$$

P_{SO_3}, etc., being the calculated percentages by volume of the constituents of the equilibrium mixture. The percentage yield may be written as :—100 $P_{SO_3}/(P_{SO_3}+P_{SO_2})$ and is therefore equal to—

$$100\,x = \frac{100\sqrt{K_f P_{O_2}}}{1+\sqrt{K_f P_{O_2}}}$$

so that K_f and x are calculated from one experiment. Since K_f constant x may also be inferred for the conjoined experiment made with another gas mixture at the same temperature, if the partial pressures of oxygen are determined by the analysis in each case. In the table the actual and calculated yields are compared in this way in three cases, nitrogen and carbon dioxide being the diluents. The agreement is a good one, and it is evident that the effect of dilution can be foretold with success. Corresponding experiments were carried out with water vapour, but water has a specific action on the catalyst, and its action is exceptional.

Knietsch also investigated the effect of pressure in the same way. A glance at equation (5) or the equation given above shows that increase of pressure increases the concentration of dioxide and trioxide in the same ratio and affects the result by raising the value of P_{O_2}. The experiments bore out this conclusion and proved beyond doubt that the Mass Action equation could be relied on here also. The results are given on page 88.

Increase of pressure and dilution with inert gases have the same effect in opposite directions. Whichever is the complication one can always find the three equilibrium partial

Pressure.	Temp. °C.	Before Reaction. Per cent. SO_2.	Per cent. O_2.	Per cent. N_2.	After Reaction. cent.	K_1.	Conversion per cent. Found.	Conversion per cent. Calculated.
Atmospheric	430	7·21	10·44	82·35	7·15	1·34	88·90	...
5·3 atmos.	430	...	...	...	36·50		99·50	99·55
Atmospheric	490	6·60	11·30	82·10	8·47	29	93·80	...
0·31 atmos.	490	...	...	...	2·67	..	90·85	89·80

pressures for a given conversion and hence, as in the case of the calculations outlined on p. 81 the value of k_f. From the curve (v.) of Fig. 11, knowing k_f, $t°$ is then found, and a few repetitions of this calculation soon define x and t in the range required.

The experiments of Knietsch which have been quoted were probably carried out in connection with a very well-known instance of the use of diluted gases. The oxidation of naphthalene to phthalic acid by means of sulphuric acid gives immense volumes of sulphur dioxide mixed with carbon dioxide. The gas is returned to contact plants and reoxidised, the other constituent having very little influence on the result. Another case which might arise is that of the burning of the spent oxide from gas purification, which contains a large quantity of carbonaceous matter.

Velocity of Reaction.

The foregoing discussion of the equilibrium in the gas-reaction of the Contact Process has shown that the dominant factor in the completeness of conversion is the temperature. It has throughout been supposed, if not expressly stated, that the amount of catalyst was amply sufficient for the work in hand. In practice, however, the maximum obtainable yield is governed by many factors. The chief is the equilibrium which obtains at the temperature employed, because the percentage yield corresponding to this cannot, in any circumstances, be exceeded. But if the weight of catalyst employed is to be, as always is the case, no more than is

necessary, another factor requires consideration—the rate at which the gases can be combined, independently of the percentage yield; in other words, the weight of trioxide which, say, 1 lb. of catalyst will produce in an hour at a given temperature.

In any given case these two factors are always at work together, and a very clear presentment of their joint action can be seen in the curves which were attached to Knietsch's classic paper of 1901. Taking first Curve 1 of Fig. 13, which represents the catalysis of 300 c.c. (per minute) of a typical pyrites burner-gas containing 7 per cent. of dioxide, 10 per cent. oxygen and 83 per cent. nitrogen, it can be seen that, as the temperature of the catalyst rises from 200° to 400°, the degree of conversion rises, rapidly at first, then more slowly until a maximum is reached about 410°, when very nearly total conversion is attained. At temperatures lower than 410° the catalyst effects only incomplete conversion, *i.e.*, the temperature is too low to allow of the necessary velocity of reaction; as it becomes hotter it converts more rapidly, and at 410° is capable of nearly complete conversion of all the gas passing through it. Above 410° the curve takes a downward slope towards the region of higher temperature. The rate of reaction, *i.e.*, the amount of trioxide which unit weight of platinum can form in a minute continues to increase (this will be shown more clearly below), but the equilibrium becomes more and more unfavourable and the maximum possible percentage yield smaller and smaller. Similar behaviour is manifested by the other curves 2, 3, 4, and 5, which represent greater volumes of gas passed over the same amount of catalyst as before. In each case, as in No. 1, there is a maximum of conversion at which the opposing effects of increasing rate of reaction and decreasing equilibrium conversion are balanced; but the maximum is less satisfactory for each case in turn, and a curve drawn through the points of maxima, slopes downwards to the right. This occurs because, to cope with each additional load, the catalyst must be given additional activity by being made hotter, and the hotter it becomes, the less satisfactory is the final result. Curve F, obtained with ferric oxide as contact-mass, falls also into this series. The right hand branches of these curves are

CONVERSION OF SULPHUR DIOXIDE (KNIETSCH).

Relation between Temperature and Yield at Various Rates of Flow.

S.B. ——— *Stoichiometric burner Gas* { 20 vol% SO_2, 10 „ O, 70 „ N

S'. ------ *Pure stoichiometric mixture*

F. -·-·-·- *Pyrites cinders* (Fe_2O_3, CuO) *as contact substance*

P. +–+– *Bits of porcelain as contact substance.*

E. –o–o– SO_3 *with porcelain contact substance.*

D. ++++++ SO_3 *in the empty porcelain tube.*

Curves 1, 2, 3, 4, 5. Burner-gas (7 per cent. SO_2, 10 per cent. O_2, 83 per cent. N_2) over platinum contact (0·5 gm. pt.).

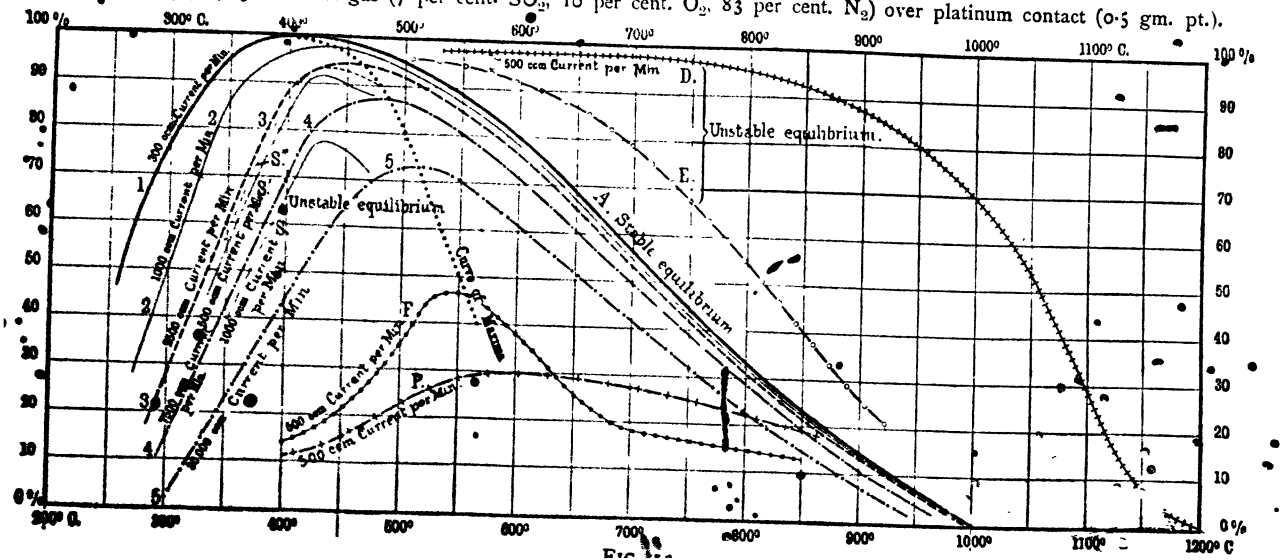


FIG.

all very close together. This means that, as the temperature increases beyond the usual range, the percentage conversion becomes more and more dependent on temperature and less on the relative weights of gas and catalyst; the velocity obtained is so high that all the experiments yield nearly the same result. There is an enormous excess of catalytic power at temperatures which are too high for it to be useful.

We can check these conclusions by calculating from the

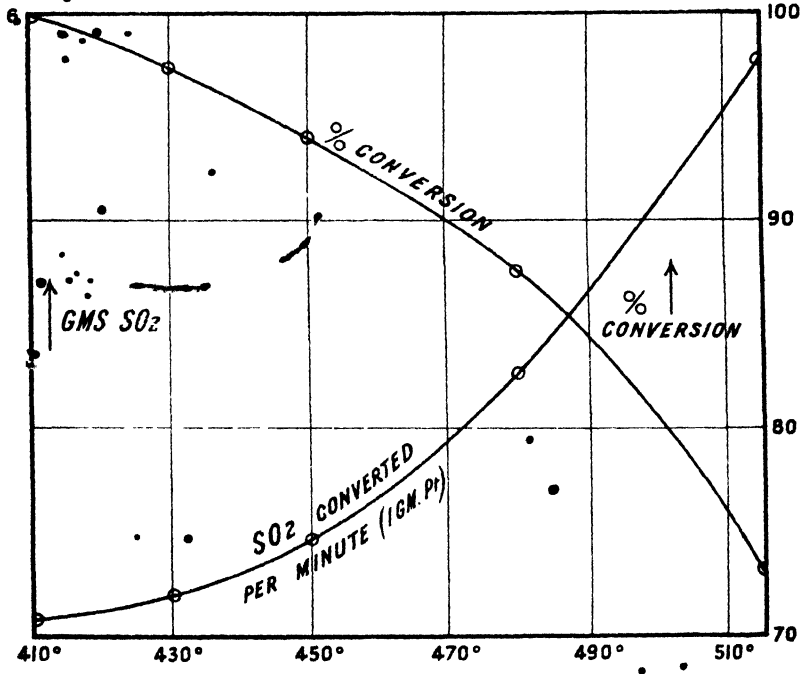


FIG. 14.—Relation between Temperature and Amount of Conversion.

maxima of the curves the weights of sulphur dioxide which unit weight of platinum was *just* able to convert in the several experiments. The platinum used was 0·5 gm. In this way we obtain the following:—

Rate, litres per min. . . .	0·3	1·0	2·5	7·5	20·0
Per cent. conversion . .	100	97·5	94	87·5	73
Temperature	410°	430°	450°	480°	515°
Grams SO_2 converted per minute by 1 gm. pt.	0·15	0·37	0·90	2·5	5·6

These figures are shown graphically in Fig. 14. The catalytic

power not only increases, but increases more and more rapidly as the temperature rises. At the same time the *percentage* conversion falls—more rapidly than it would if the conditions were those of equilibrium. This is shown by the upper curve, which corresponds to the dotted curve of maxima in Fig. 13.

Knietsch also presented his results in a somewhat different form, as in Fig. 15. Each curve in this case corresponds to the relation between conversion and amount of platinum (or time of contact with a constant quantity). The relative time required to attain a certain conversion at a given temperature can at once be read off. At 300° the maximum conversion is not attainable under the conditions of the experiment within the time indicated. As temperature rises high conversions are reached more rapidly, until at 450° the curve is at first almost coincident with the vertical axis of the diagram. This curve reaches its maximum before any other curve does so, and the maximum stands as high as any other. In this is the foundation of the oft-repeated empirical statement that the platinum contact chambers of a Contact Plant work best at 450°. Further information—a tabulation of the various weights of sulphur dioxide which are converted by one pound of platinum in different plants, will be found in Chapter IV.

The velocity of the sulphur dioxide-oxygen reaction was investigated by Bodländer and Köppen.[1] The same subject was taken up by Bodenstein and Fink in what has now become one of the classical studies of heterogeneous catalysis.[2] These investigators passed the mixture of gases, carefully dried over sulphuric acid, into a hard glass tube containing a roll of platinum gauze. Special precautions were taken to detect any accidental poisoning. The rate of reaction was observed by measuring the decrease of pressure, the volume being kept constant. In order to obtain easily measurable velocities, the tube was maintained at some temperature between 155° and 248°, and most of the experiments were made at 248°.

The results obtained have very considerable bearing on the chemical mechanism of catalysis by platinum, and will be more fully discussed in connection with the nature of this phenomenon, in the next chapter. It may be noted for our

[1] *Z. Elektrochem.*, 1903, 9, 559, 787.
[2] *Z. physik. Chem.*, 1907, 60, 1.

CONVERSION OF SULPHUR DIOXIDE (KNIETSCH).

Relation between Conversion and Time of Reaction, at Various Temperatures.

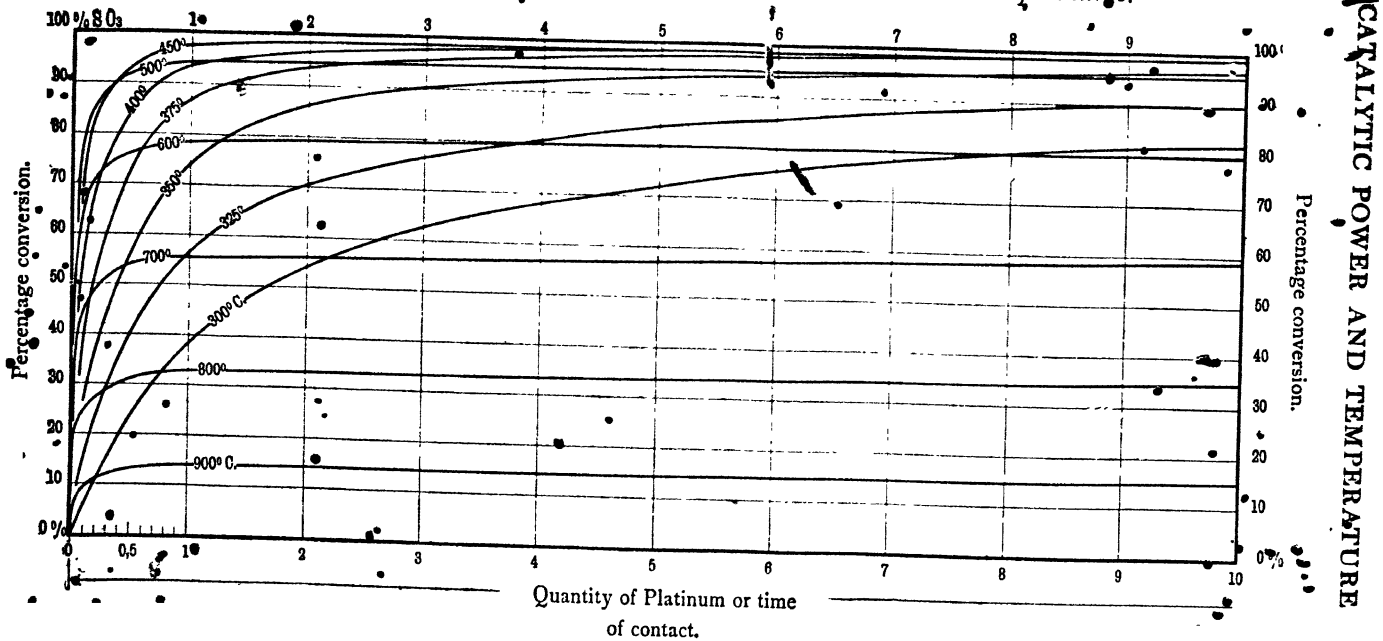


FIG. 15.

present purpose, that the reaction did not proceed as a gas reaction between three molecules might perhaps be expected to do, but followed a course which may be represented by—

$$\frac{dx}{dt} = k\frac{(a-x)}{x^{\frac{1}{2}}},$$

in which a is the amount of dioxide (in molecules per litre) originally present and x the amount converted in t minutes, k being a constant. In other words the rate of reaction after t minutes had elapsed was directly proportional to the amount of dioxide remaining and inversely proportional to the square root of the trioxide formed. The reaction was accordingly found to slow down as the trioxide accumulated in the system, and—what is more remarkable—the concentration of the oxygen was without any influence whatever within wide limits. If, however, less oxygen was present than the ratio $2SO_2 : O_2$, the function k no longer remained constant and the rate of reaction became abnormally slow. It has previously been pointed out that above a limit rather higher than this the concentration of oxygen has only a slight effect on the yield attainable at equilibrium, and that at this point defect of oxygen begins to make itself felt in this case also. We are therefore justified in thinking (if Bodenstein's results can be interpreted for a higher temperature in the same sense), that in any usual case, alteration in the proportion of oxygen can have only slight influence on the reaction, either from the point of view of velocity or from that of equilibrium.

The temperature coefficient of the reaction was found to be 1·22 for every 10°.

Determination of the Equilibrium Constants.

In the foregoing discussion reliable values of the equilibrium constant at various temperatures have been taken for granted. Since such values are essential for precise knowledge and calculation, it is of great interest to record the methods which have been employed and to compare their results.

Knietsch was the first investigator to obtain quantitative information regarding the equilibrium. His results are presented, with much other matter relative to the Contact Process, in his lecture to the German Chemical Society of

1901.[1] His object was rather to ascertain what proportion of dioxide in various gas mixtures could be converted with a given quantity of platinum at speeds comparable with these technically necessary, than to determine the exact equilibrium. The usual "dynamic" method was employed, the gas mixture being passed through a tube heated in an electric furnace. The first half of the tube was empty and served to preheat the gas; the second half contained 0·5 gm. of platinum on 5 to 10 gm. of asbestos.

The results of these experiments have already been discussed. It is clear that they are not available as a whole for the purpose in view, but there is some evidence that at the lowest rate of passage (Curve 1, Fig. 13) the platinum was sufficient to secure equilibrium. The conversion was practically 100 per cent. at 400° so that sufficient platinum must have been present to secure equilibrium at higher temperatures, for if the temperature were above 400°, the catalyst must have been even more active. From this series of results a series of equilibrium constants was calculated by Bodländer and Köppen[2] and by D'Ans.[3] The results of D'Ans, recalculated by Haber for k_f are given in the next table. Two other measurements, made by sealing up gas mixtures with platinum in glass tubes, were reported from the work of the *Farbwerke Höchst* about 1902, but differ widely from accepted values.

Measurements were also made by Bödlander and Köppen by a novel method designed for the end in view. Two similar quartz vessels, each containing a roll of platinum wire-netting, were filled, one with air, the other with the gas mixture under examination. Both vessels were heated to the required temperature, and in each case the pressure inside the vessel was allowed to equal one atmosphere. The temperature was then allowed to fall to about 410°, so that the combination of the sulphur dioxide with oxygen became practically quantitative. In the case of the vessel containing air the contraction was due solely to cooling; in the other it was due also to combination, and the corrected contraction was a measure of the amount of trioxide dissociated on heating from 410° to the temperature used.

[1] *Ber.*, 1901, **34**, 4069-4115. [2] *Z. Elektrochem.*, 1903, **9**, 787.
[3] Haber, *Thermodynamics of Technical Gas-Reactions*, 1908, 193.

It was stated that temperatures higher than 650° could not be employed on account of absorption of oxygen by the platinum. The gas mixtures all contained more than 30 per cent. of sulphur dioxide. The following figures, given by Haber show the results, together with the values calculated from Knietsch's work.

$t°$.	k_p (Bodlander).	k_p (Knietsch).
450		187·7
500		72·3
515	65·4	
533	28·4 (average)	
600	...	14·9
610	10·6 (average)	
650	...	(4·45
700	4·84	
800	1·81	
900	0·57	

The two sets of values are in fair general agreement. It is possible to test their consistency, although not their accuracy as a whole, by calculating from them the molecular heat of formation of trioxide (at constant pressure). This quantity is related to k_p by the equation—

$$\frac{d(\log_e k_p)}{dT} = \frac{Q_p}{2RT^2},$$

R being in gram-calories, which on integration and with common logarithms becomes—

$$\log_{10} k_p - \log_{10} k'_p = \frac{Q_p}{9.14}\left(\frac{1}{T} - \frac{1}{T'}\right),$$

in which T and T' are two absolute temperatures not so far apart that Q_p changes considerably from one to the other. Bodländer and Köppen[1] found that by this test Knietsch's figures gave very irregular values for the reaction heat. His

[1] Writing concentration terms, they calculated the values of Q_v by the usual expression involving K_c, viz., $\log_e K_c - \log_e K'_c = \frac{Q_v}{R}\left(\frac{1}{T'} - \frac{1}{T}\right)$. Q_p, however, is a quantity of more practical interest and in the case of this reaction has the advantage, for such purposes as the above, of being far less variable with temperature than is Q_v. Of course $Q_p = Q_v + 0{\cdot}99T$.

series of results cannot therefore be accepted for the purpose in view. Their own figures give the reaction heat Q_p as 26·3 kilocalories between 515° and 553°, and practically the same between 553° and 610°, but between 610° and 650° it appears to have risen to 31·2. An experimental disturbance is known to have interfered with the equilibrium determination at the higher temperatures. These investigations, therefore, do not provide us with what we want.

The later investigation of Knietsch has already been noted (see p. 86). The experimental method was an improved one. Gas mixtures from an adjacent plant were used. Their composition was not constant but averaged the same over different periods of test—usually of an hour each. The electric furnace for heating the catalyst worked with alternating current in such a way that current and intensity of heat were far more nearly proportional than in the older types using direct current. Great care was taken to secure constancy of the experimental conditions, and the plant gases were led over the heated catalyst for fourteen days before it was used. Each experiment lasted eight to ten hours. Samples of gas before and after conversion were passed into iodine solution, and the excess of iodine estimated. Particulars of most of the results have been given. Another series was made with burner-gas mixed with its own volume of air, at 430°, 560°, and 640°. The collected results are given in the table on p. 86. Just as in the first series of 1901 Knietsch was concerned more with the yield obtainable under stated conditions of temperature and rate of flow than with the actual equilibrium. The second series probably exceeds the former in precision.

The most reliable data we have for the equilibrium functions are due to the work of Bodenstein and Pohl.[1] For a full description of these careful and elaborate experiments reference should be made to the original paper. A brief account of the method employed will be of interest.

Pure oxygen was generated by electrolysis of a solution of potash or barium hydroxide and was freed from traces of hydrogen by passage over palladium. The rate of evolution of oxygen could be satisfactorily regulated by adjusting the potential applied to the electrolytic cell. Sulphur dioxide

[1] *Z. Electrochem*, 1905, 11, 373.

was liquefied and the containing vessel was immersed in a bath, the temperature of which was raised by means of an automatic regulator as the atmospheric pressure rose, so that the additional pressure of gas remained the same, whatever the atmospheric pressure might be. The sulphur dioxide was allowed to leave the containing vessel by one or more calibrated jets, the capacities of which were proportional to the numbers 1, 2, 4, 6, and 15. By using various combinations of these jets almost any desirable rate of flow could be obtained. The gases so obtained were mixed, nitrogen or air being added when required; the percentage of sulphur dioxide was estimated in a sample withdrawn from the main stream, and the mixture was then passed into the reaction tube. This was of quartz and was constructed with two bulbs, each filled with platinised asbestos. The first served to ensure almost complete combination, and the gases, on reaching the second, in which final equilibrium was attained, gave out or absorbed scarcely any heat, so that the conditions were in favour of an even temperature in the second bulb. Bodenstein and Pohl point out that, since the ends of an electric furnace are in general cooler than the centre, combination of dioxide and oxygen may occur towards the end of the tube, where the temperature is lower than the thermocouple indicates. They believe that the earlier results of Knietsch were vitiated in this way, and provided against this source of error in their own experiments by making their bulbs of small length in comparison with their diameter, and making the tube by which the gases left the reaction vessel of very small bore. If the fact that temperature diminishes from centre to end of the furnace is borne in mind, it can readily be seen that these investigators, by altering the position of their reaction tube relative to the furnace, could make either the first or the second tube the hotter, and could therefore cause final equilibrium to be approached by a slight combination, or a slight dissociation, respectively.

After reaction the gases were again analysed, in this instance by estimation of their contents of dioxide and of total acid. The results so obtained were sufficient for calculating conversions, and were in excellent agreement with the preliminary check analyses. As an instance, the figures

for the experiments carried out at 727° C. are reproduced below:—

T (abs.)	Direction.	Ratio (initial) $2SO_2 : O_2 : N_2$.	Per cent. Conversion.	K_c.
1003	C	0·21 : 1 : 0	59·6	$3·49 \times 10^{-3}$
1001	C	0·54 : 1 : 0	53·6	$3·51 \times 10^{-3}$
1000	C	0·62 : 1 : 0	52·2	$3·59 \times 10^{-3}$
1000	C	1·14 : 1 : 0	44·4	$3·44 \times 10^{-3}$
1000	C	1·20 : 1 : 0	43·7	$3·48 \times 10^{-3}$
1000	C	1·32 : 1 : 0	42·3	$3·67 \times 10^{-3}$
1000	C	1·68 : 1 : 0	37·2	$3·50 \times 10^{-3}$
1000	C	1·68 : 1 : 0	37·1	$3·52 \times 10^{-3}$
1001	C	3·97 : 1 : 0	20·8	$3·67 \times 10^{-3}$
998	C	1·23 : 1 : 3·76	35·3	$3·62 \times 10^{-3}$
997	C	1·23 : 1 : 3·76	35·8	$3·58 \times 10^{-3}$
1001	C	1·31 : 1 : 3·76	34·1	$3·54 \times 10^{-3}$
1001	C	1·55 : 1 : 3·76	32·3	$3·52 \times 10^{-3}$
1000	D	0·53 : 1 : C.	54·4	$3·43 \times 10^{-3}$
				Mean, $3·54 \times 10^{-3}$

In column 2 "C" denotes that equilibrium was attained by a slight combination, *i.e.*, the second bulb was the cooler. "D" denotes the reverse. The series of equilibrium constants obtained in these experiments is remarkably even; such variations as do exist are due mainly to slight differences of temperature between one experiment and another of the same series. The initial proportions of the gases cover a wide range and the investigators conclude with the remark: "The equilibrium of the Contact Process obeys the demands of the principles of Mass Action and of thermodynamics in such an excellent way that it can serve as one of the best examples for illustrating them."

The complete series of results is set out below. Given originally in terms of K_c, they have been calculated to k_p.

Equilibrium Constants—Bodenstein.

t° C.	k_p found.	k_p calculated.	Q_p kilocalories.
528	31·3	31·6	
579	13·8	13·4	22·8 (600°)
627	6·54	6·56	
680	3·24	3·16	22·7 (700°)
727	1·860	1·840	
789	0·956	0·979	22·6 (808°)
832	0·627	0·642	
897	0·358	0·355	

It will be seen that the reaction heat at constant pressure increases about 100 calories for every 100° decrease of temperature. At about 0° it should therefore have a value about 23·4, which is not very far from Berthelot's value of 22·6 at 18°. Bodenstein and Pohl represent their observed values of K_c by an equation[1] derived from that of Van't Hoff, in which the constants are obtained from the values of the reaction heat (Q_v), allowance being made for the variation of this quantity with temperature. The correspondence between calculated and observed values is very close, and in view of the approximation of the known and calculated values of the reaction heat at ordinary temperatures, the equation should be valid throughout the whole range in which it is required.

Transformed to make use of the function k_p, the equation is (with common logarithms)—

$$\log k_p = \frac{5186.5}{T} + 0.611 \log T - 6.7497 \quad (1).$$

This expression accordingly represents our most complete and reliable knowledge of the equilibrium constant, but it is unfortunately useless for finding T (the absolute temperature at which any given equilibrium will hold), and the process of calculation outlined on p. 81, where we begin with a given gas mixture and assume a certain conversion, cannot be completed by its means. Haber has suggested the use of the following:—

$$\log_e k_p = \frac{21700}{4.571 T} - 20.4 \quad (2).$$

From this T can be calculated, but the equation is not very accurate, for the reaction-heat is supposed to be constant. The simplest method is nevertheless to make use of it and correct the values obtained from it for the divergence of the equation from (1). The corrections which must be added to T obtained from Haber's equation in order to bring it to the value which is involved in (1), are given below to the nearest 0·5° C.

Haber's T	400°	420°	440°	460°	480°	500°	520°	540°	560°	580°	600°
Add	9	8·5	7·5	7	6	5·5	5	4	3·5	3	2

[1] $\log_e K_c = \frac{10373}{T} - 2.222 \log_e T + 14.585.$

The curves of Fig. 11 connecting k_p and $t°$ and showing the conversions attainable with various gas mixtures have been obtained by calculation and correction in this way.

Although the measurements which have been described are undoubtedly the best data we have regarding the equilibrium, it will be noticed that the lowest temperature at which any series was made is 528°, and that consequently the values we require have to be obtained by extrapolation in the most important region. The work has much to give us confidence in the extrapolation, but some satisfaction can nevertheless be derived from the fact that the extrapolated values, and those deduced from Knietsch's second set of experiments, agree fairly well.

	480°	460°	470°	490°	560°	640°
k_p, Knietsch (observed average)	252	135	86	63	18	5
k_p (B. and P.) calculated .	232	122	94	64	16	5

A comparison with the first series of Knietsch shows a wide divergence, and in most cases the constants are not even of the same order. It is interesting to note that these determinations (which have been widely accepted) are, according to Bodenstein and Pohl, inaccurate by 15° at 500°, and by an increasing amount as the temperature rises; by 26° at 600°; 50° at 700°; and so on. In every case Knietsch's figures overestimate the possible conversion. It has been pointed out that the conditions under which the experiments were made—uneven temperature along the reaction tube—would cause more complete combination to occur at the cool ends than in the hot centre.

Bodenstein's figures are quite discordant with those of Bodländer and Köppen, but agree well—an interesting point in connection with the general nature of catalysis which has been already touched on—with those obtained by Lunge and Reinhardt, over ferric oxide.

The Effect of Ultra-violet Light.

The reaction between sulphur dioxide and oxygen is catalysed by ultra-violet light, and a stationary state is reached in which, as in the thermal equilibrium, the opposing reactions of combination and dissociation are balanced. This "photo-

stationary state," however, may be, and is in this case, markedly different from the thermal equilibrium.

The matter was studied by Coehn,[1] who found that oxidation of sulphur dioxide occurred at the ordinary temperature. The same influence, also at room temperature, causes the trioxide to split up in the absence of oxygen, and form dioxide and oxygen. Quartz glass tubes were filled with the gases and exposed to the rays in the axis of a mercury lamp of special design, so that they received radiation from the lamp on all sides. The temperature was regulated by immersing the lamp in water, and by passing water through the space between the inner quartz tube and the reaction tube.

At about 50° the reaction was found to be a comparatively slow one, but raising the temperature increases its rate very greatly. Data from experiments made at 50° and 160° are as follows:—

$t=160°$.			$t=50°$.		
Time.	Ratio SO_2/O_2.	Final per cent. SO_3.	Time.	Ratio SO_2/O_2.	Final per cent. SO_3.
5 mins.	1·6	20·0	5 mins.	1·6	2·5
15 „	1·4	39·5	15 „	1·6	13·6
1 hour	1·3	66·0	1 hour	1·5	28·7
2 hours	1·2	65·0	8 hours	1·5	60·7
6 „	1·3	68·0	...	...	...

The conversion of 65 per cent. obtained after one hour is not much increased by further exposure—the "photo-stationary state" has been reached. At 160° if the *thermal* equilibrium could be attained—for instance by a much more active catalyst than any so far discovered—the conversion would be practically 100 per cent. It is clear that the two equilibria differ widely. The same point, as regards the photo-chemical change, was reached by exposing trioxide sealed up in a quartz tube to the rays—about 35 per cent. of the trioxide was dissociated. Other experiments made clear the very remarkable fact that increased temperature, although increasing the reaction velocity and consequently the rate of approach to equilibrium, did not cause the equilibrium to shift in either direction. For any

[1] *Z. physik. Chem.*, 1907, **18**, 545, and 1910, **70**, 88.

given gas mixture the conversion is independent of temperature, and it is therefore possible at high temperatures to obtain higher yields by the photo-chemical than by the thermal method. For instance, at 800° if thirteen volumes of oxygen are present to one of dioxide, 80 per cent. is converted. The thermal conversion gives only 44 per cent. Experiments made with a lamp more adapted to technical development showed conversion ranging from 67 to 90 per cent., according to the SO_2/O_2 ratio, the rate of passage being 100 to 150 c.c. of gas per minute. The temperature coefficient of velocity was found to be about 1·2 for 10°—nearly the same as for a thermal catalytic process.

The contrast between the action of a solid catalyst and of the ultra-violet rays is a most interesting one. It is evident that the rays are capable of doing work in opposition to the chemical forces, for at the lower temperatures the equilibrium could have moved, *e.g.*, by the action of platinum, to a point representing further combination and loss of free energy. It is not easy to estimate the possibility of the process becoming technically important. Success would depend on a more economical production of the rays than is possible at present. Coehn passed 6 amperes through his lamp. The position of the photo-stationary point depends on the intensity of the illumination and appears to move towards more complete conversion as the intensity falls. Coehn and Becker, in a patent for the use of this method (Ger. P. 217722), state that the intensity of the light must be as small as possible, and the lamps must not be of the type most appropriate for lighting purposes, but must be worked with a small pressure of mercury vapour. By reducing the light the velocity of reaction is reduced also, and to increase this the system is heated to 300° or so. Burner-gas may be employed.

The application of ultra-violet light to this reaction has also been the subject of other patents (B. P. 10881 of 1904; 17520 of 1908). Although it is at present a matter mainly of scientific interest, it would be rash to say that its technical development is altogether improbable.

CHAPTER IV

CATALYSIS AND CONTACT-MASS

PART I.—CATALYSTS AND THEIR ACTION.

THE property of catalysing the sulphur dioxide reaction is possessed by practically all solid substances which do not melt or vaporise at the temperature of reaction, in greater or less degree. Smooth glass surfaces have a very slow action, porcelain and silica a more rapid one, and between the activity of these comparatively inert substances and that of platinum all gradations could, if necessary, be provided by various metals, their oxides and salts.

It would not have been possible to discuss the gas reaction fully in Chapter III. without indicating the general behaviour of platinum as a contact material. On account of its pre-eminent position the discussion of this metal and the various contact-masses made with it will be deferred until the ground has been cleared by consideration of the general nature of catalysis and the properties and general behaviour of other catalysts.

Phenomena and Theories of Catalysis.

The selection of a catalyst for a given chemical reaction has been, and still is mainly empirical. There is no certain method other than trying as many substances as possible, and the patent literature show that such trials have been widely if not altogether thoroughly made. There are, nevertheless signs that general principles may emerge from the mass of facts to form a guide to the applicability of catalysts. The physical phenomena which accompany catalysis at solid surfaces, and indeed are an essential part of it, are becoming more widely known. A brief account of the theories which have been advanced, and the salient facts on which they are

based, may therefore be of use. It will be restricted to the reaction in view.

The earlier workers had no difficulty in explaining the catalytic action of such substances as ferric oxide, for the supposition that ferric sulphate was being formed and decomposed simultaneously was a very plausible one, supported by much evidence. The intermediate compound-theory could not be so readily applied to platinum. Platinum was generally supposed to have no affinity for oxygen at the temperature of the reaction, and to act by condensing the gases in its pores. The theory that a transitory platinum oxide was the active agent was first suggested by Engler and Wöhler,[1] who found that platinum black contained an oxide which acts as an oxygen-carrier in certain reactions. At first a peroxide of platinum was supposed to be present in platinum catalysis; later on it was claimed that the ordinary oxide PtO had all the required properties. Some years later it was proved[2] that the substance PtO could not exert any effect at the usual temperatures of the reaction, since it was reduced to platinum by the sulphur dioxide before the reaction was well begun. Reduction is appreciable at 130° and very rapid at 400°. Even before reduction has set in, the action of the oxide is only about one-fifth as vigorous as that of the metal. Platinum oxide as the active agent must therefore be excluded, and it is difficult to suppose that *any* oxide, the formation of which is exothermic, can function in this way. An endothermic oxide, however, might have the function of an oxygen-carrier, and would tend to increase in amount as the temperature rose, so that catalysis would increase with temperature as is of course the case. It was suggested that such an oxide may dissolve in the platinum in a state of solid solution, the gas also being soluble.[3] On this assumption the function of a catalyst is to form a solid solution in which the reaction proceeds.

[1] *Z. anorg. Chem.*, 1901, **29**, 1.

[2] Wöhler, Foss, and Plüddemann, *Ber.*, 1906, **39**, 3538.

[3] Bodenstein argued that no endothermic compound could be present since the catalytic activity of platinum *decreased* above a certain temperature, but there is no evidence of such decrease, only of a continuous *increase* if activity be estimated by the weight of gas converted (*Z. physik. Chem.*, 1907, **60**, 43).

A novel suggestion was put forward by Wieland,[1] who found that palladium black, in the absence of oxygen, oxidised moist sulphur dioxide. It is known that traces of water are essential for the catalysis by platinum, and is suggested that this water is alternately dehydrogenated and reformed,

$$SO_2 + H_2O \longrightarrow SO_3 + H_2, \quad 2H_2 + O_2 \longrightarrow 2H_2O,$$

oxygen being always present in the usual case.

In the other case which has been much discussed,—that of ferric oxide—it was known that the catalyst forms more than one compound with the trioxide produced. Ferric sulphate decomposes in the same temperature range in which the oxide is active as a catalyst. It was therefore very natural to suppose that the interaction of the oxide, oxygen, and sulphur dioxide gave ferric sulphate,

$$2Fe_2O_3 + 6SO_2 + 3O_2 \longrightarrow 2Fe_2(SO_4)_3,$$

which was considered as simultaneously decomposing into ferric oxide and sulphur trioxide, a state of equilibrium in which the opposing reactions are balanced being established at each temperature. Another series of changes also considered as possible, is given in the equation—

$$3Fe_2O_3 + SO_2 \longrightarrow 2Fe_3O_4 + SO_3, \text{ and } 4Fe_3O_4 + O_2 = 6Fe_2O_3.$$

There is no doubt that these reactions did actually proceed under suitable conditions, and in fact they appear to be important in the operation of iron oxide contacts; but that they were in themselves the means of producing catalysis was by no means certain. The subject was investigated by Keppeler and D'Ans,[2] who determined the conditions of equilibrium for the gases above ferric oxide and measured the partial pressure of trioxide produced by the dissociation of the sulphate. The experimental method was to pass mixtures of sulphur dioxide and air or nitrogen, corresponding to technical mixtures, over the heated catalyst. Absorption of sulphur dioxide and oxygen *together* begins at about 230°, and is rapid enough at 500° to allow the gas-equilibrium to be studied. It was found that the concentration of trioxide was always higher than that

[1] *Ber.*, 1912, 45, 685.

[2] *Z. angew. Chem.*, 1908, 21, 532 and 577; *Z. physik. Chem.*, 1908, 62, 89.

corresponding to equilibrium with the dissociating sulphate; in other words, that sulphur trioxide forms first and combines afterwards. The rate of formation of trioxide is far greater, below 640°, than the rate of formation of the sulphate. Sulphur dioxide alone has no chemical action on the oxide below 600°, and acts only very slowly at higher temperatures, but this gas is found to be absorbed by the oxide to about the same extent as by platinum. The conclusion is, therefore, that the chemical transformations which ferric oxide may undergo into ferric sulphate and similar compounds, have little to do with its catalytic action.

We are therefore driven back, even in this instance, where the intermediate chemical compound is known certainly to be present during the catalysis, to some physical explanation of the catalytic effect. Faraday, in 1834, was the first to suggest such an idea. He thought that the reacting gases were absorbed bodily into the metal. J. J. Thomson suggested that capillarity is the cause of the effect, which is therefore a surface phenomenon. The idea that catalysis by solids takes place in the condensed layer which is formed by the attraction of the reactants to the surface, *i.e.*, in the adsorbed material, has proved not only defensible but fruitful. Adsorption is a well recognised phenomenon and there is considerable evidence connecting it with catalytic action. In many cases the surface of the catalyst is submitted during the reaction to powerful forces, and a rapid alteration may take place, resulting as in the case of the platinum gauze used for the oxidation of ammonia, in a drastic pitting and sprouting of the whole surface.[1] Wöhler and others who examined the contact action of various oxides of chromium, copper, aluminium, and titanium believed that the catalytic efficiencies of differently prepared specimens of the same oxide were in proportion to their adsorbing capacities, but found that this relation did not hold when different oxides were compared. More recently very interesting work by Taylor and Burns[2] has established that there are a number of cases in which catalytic activity is correlated with the absorption of one or both of the reactants. The adsorption of hydrogen, carbon monoxide, carbon dioxide,

[1] Imison and Russell, *J. Soc. Chem. Ind.* (*Trans.*), 1922, 41, 40.

[2] *J. Amer. Chem. Soc.*, 1921, 43, 1273.

and ethylene by finely divided nickel, cobalt, iron, copper, palladium, and platinum is a specific property, quite different in nature from the adsorption by inert adsorbents such as charcoal. The amount of adsorption is a function of the mode of preparation and is less pronounced the higher the temperature at which the reduced metal is made. In the instances of nickel and hydrogen, and of copper and carbon monoxide, adsorption increases rapidly with partial pressures up to 300 mm. and beyond this point becomes practically constant. Destruction of the catalytic activity (*e.g.* by overheating) is accompanied by almost complete suppression of the power of adsorption, and the adsorptive capacity may be taken as an indication of the temperature at which the reaction can be carried out.

We may now revert to the study made by Bodenstein and Fink of the velocity of reaction of the sulphur dioxide-oxygen reaction catalysed by platinum,[1] already referred to in Chapter III. It will be remembered that the velocity at 248° was found to be independent of the oxygen concentration, and proportional to the concentration of the unconverted dioxide, and that as the amount of trioxide accumulated the velocity slowed down. If it is supposed that the trioxide formed is concentrated on the surface of the catalyst by adsorption, the reacting gases would be forced to penetrate this layer to be catalysed, and the reaction would be retarded; and since the amount of a substance adsorbed depends generally on the concentration, the higher the concentration of trioxide the greater would be the retarding effect. It was proved by actual experiment that sulphur trioxide vapour is adsorbed by platinum, although, probably on account of slight poisoning, constant values could not be obtained. It is known that sulphur dioxide is also slightly adsorbed.

The temperature coefficient of the reaction was found to be 1·22 for 10°. In chemical reactions which occur in solution the rate of reaction is approximately doubled for every 10° increase of temperature. It is even found that the coefficient is about the same as this for reactions in solution which are catalysed by colloidal metals, *e.g.*, the decomposition of hydrogen peroxide by colloidal platinum. Clearly catalysis at the

[1] *Z. physik. Chem.*, 1907, 60, 1.

platinum surface in the gas-reaction must be retarded by some factor which is absent in other reactions. This factor can hardly be the adsorption itself, for adsorption is known to occur with extremely great rapidity, and we are forced to assume that the governing condition is the rate at which the gases can diffuse through the adsorbed layer on the surface of the catalyst. Diffusion processes are known to have a much lower temperature coefficient than typical chemical reactions.

This view of catalysis need not be restricted to platinum, for Keppeler and D'Ans arrived at practically the same conclusions in regard to ferric oxide, and Berl[1] found the same phenomena evident in the case of arsenic pentoxide; the reaction coefficient was 1·21 between 295° and 340° and 1·19 between 340° and 380° for each increase of 10°.

Adsorption in solid catalysis is not so much a theory as a fact. Without in any way *explaining* the catalysis it gives us a clearer picture of the interaction of the substances concerned. There are well-known cases of catalysis in which the assumption of intermediate chemical combination can and must be made, to give a reasonable explanation, but this does not appear to be such a case. The subject is a wide one, of steadily increasing interest and importance. No attempt has been made here to answer the question—What is the nature of the catalytic influence?—or, Is adsorption itself due to the attraction of chemical valencies? The Radiation Theory, the nature of the absorption layer and kindred subjects are beyond our scope.

Physical Condition of the Catalyst.—Since catalysis is a phenomenon depending on solid surfaces, the state of the surface—its extent and accessibility to the reacting gases is a matter of the highest importance. There is a great variety of methods of making this surface as large as possible, ranging from simple abrasion of the massive substance to deposition in a state of extreme division on a more or less porous, inactive support. A good example of this variety is seen in the procedures possible in the case of vanadium oxide—a substance which not only has considerable importance for the contact process but is the basis of the more recent method of oxidising naphthalene to phthalic acid, and is of almost general applica-

[1] *Z. anorg. Chem.*, 1905, 44, 267.

bility for catalytic oxidations. The oxide can be broken up and used in the massive state; it can be deposited on an inactive support such as asbestos by soaking the support in ammonium vanadate solution and heating, or the massive oxide can be caused to sinter and pit by previously heating under the conditions of its actual use, to a temperature higher than the normal, acquiring a greatly increased activity.

This sintering effect is a very frequent one, and is generally associated, in the case of very finely divided substances, with a loss of activity and not with a gain, as in the instance just quoted (in which, it should be noted, the original material is very coarse). The metals copper, gold, silver, platinum, palladium, and iron have each, in a fine state of division, been observed to show incipient melting at temperatures far below their melting-points.[1]

Now, each of these metals is the more active, the lower the temperature at which its compound is reduced, that is, in all probability, the less the opportunity given to the particles to coalesce in the observed way during the reduction. On first using a finely divided platinum catalyst abnormal activity is often shown. This may well be due to the evolution of occluded gases, leading to still further division of the surface. As the catalyst continues in use the activity falls to a steady and normal value. It is most probably due to the very high melting-point of platinum that the activity of this metal can remain unimpaired for so long, the temperature required for appreciable sintering to occur being unusually high.

The methods of producing a fine stage of division, and the production of the various supports, will be given with the description of the various contact substances in use. It is advisable to conclude this general treatment of the subject by a brief discussion of the influence of impurities on the contact reaction between sulphur dioxide and oxygen.

Influence of Water Vapour.—Striking observations were made on this subject by Russell and Norman Smith in 1900.[2] They found that even at the ordinary temperature certain oxides—manganese and lead peroxides, ferric and chromium oxides—would each cause sulphur dioxide and oxygen to unite

[1] Wright and Smith, *J. Chem. Soc. Trans.*, 1921, 119, 1683.

[2] *J. Chem. Soc. Trans.*, 1900, 77, 340.

in proportion to the extent of surface presented. The amount of combination, in the case of a precipitated oxide, increased as the substance dried in the air, or was moderately heated to dryness. Manganese dioxide was found to convert ·20 per cent. of the sulphur dioxide present. In all cases gaseous oxygen was taken up and not merely passed on from the metallic oxide to the sulphur dioxide.

When any of the materials had been dried by means of phosphorus pentoxide for several days no combination took place. It might seem that this were due to the removal of the film of water on the surface of the oxide, the reaction taking place in this film, if it were not that platinum at 450° shows the same behaviour. Platinised pumice was heated at 400° to 450°, and oxygen was passed over it and over pentoxide, back and forwards for three weeks. Sulphur dioxide was dried at the same time. On mixing the gases and passing them over the platinum the action was so slow that a perceptible diminution of volume took place only after twenty-four hours. The many striking instances of the indispensability of water in chemical reactions which are to be found in the work of Baker come at once to mind.

It has often been asserted, as will be seen in connection with arsenic, ferric, and vanadic oxides, that the drying of gases so far as it can be carried by concentrated sulphuric acid, is advantageous, but that further drying with phosphorus pentoxide, as in the experiments of Russell and Smith, leads to diminished activity. The question arises whether the presence of water is unfavourable to the action of platinum when considerable amounts are present. In practice, the presence of water may imply that sulphuric acid, and other deleterious substances, are reaching the contact-mass from the burners, and it is known that water has of itself an injurious action. Knietsch, however, in his second paper, recording the experiments on the influence of inert gases on the gas-equilibrium, gives data of two runs made with burner-gas to which had been added water vapour.

Per cent. SO_2 in Gas.	Per cent. Water Vapour Added.	Conversion. Found.	Conversion. Calculated.	
7·2	13·5	96·4	96·6	$T° = 460°$
6·6	26·7	96·8	97·5	

(For the method of finding the calculated values, see Chapter III.). It should appear that water had little influence on the equilibrium at this temperature. We have no data to decide whether it alters the velocity. So far as experiments on a small scale are concerned, it is certainly possible to work with dried or undried gases without any difference in the performance of the platinum,[1] but in practice the effect of water is always a bad one.

The Poisoning of Catalysts.—It is impossible to complete a survey of the physical phenomena of this branch of catalysis without reference to the subject of catalyst poisoning. Platinum is extremely sensitive to the action of certain substances, very small amounts of which seriously impair its activity or suppress it altogether. This fact constitutes the outstanding difficulty of the Contact Process as a technical operation. The investigations of Bredig and others on the decomposition of hydrogen peroxide by colloidal platinum, and the effect of traces of "poisonous" material are at once recalled. A concentration of iodine equal to 2×10^{-6} was in that case sufficient to reduce the activity to one half.

The most dangerous and frequent poison is arsenic. Its action on the catalyst is to a great extent a permanent one, and although more or less satisfactory means have been devised to re-induce activity in the platinum, a severe dose of poison always involves the recovery of the platinum from the contaminated mass. How the arsenic and other poisons find their way to the catalyst, and the means of preventing them doing so, will be discussed at a later stage (Chapter VI.).

Chlorine, iodine, hydrochloric acid, silicon tetrafluoride, sulphur, and lead sulphate have each an adverse action; but we are hardly justified, in the strict sense of the word, in calling all these substances poisons, for there are two methods in which the activity of the catalyst can be reduced in this way: first by the access of a substance which has a specific poisoning action, and secondly by a deposition of solid matter on the catalyst, which hinders the diffusion of the reacting gases to its surface. It would appear that compounds of arsenic, antimony, tellurium, and selenium have a permanent specific action; chlorine and hydrochloric acid a temporary one; and that the other substances exert mainly a mechanical action,

[1] Reese, *J. Soc. Chem. Ind.*, 1903, **22**, 351.

although too little is known of the subject for this classification to be laid down at all rigidly.

There is no generally received explanation of this specific poisoning effect. In the view of Opl[1] a glassy coating was formed on the surface of the platinum of the compound $As_2O_3, 3SO_3$, which had been found occasionally in the dust chambers of pyrites burners. Bodenstein has recorded the speculation that the influence of the poisons on the adsorption of the trioxide at the surface may be the underlying cause. In mild cases of poisoning there may be mechanical adherence of impurity which hinders diffusion; but to account for drastic cases this assumption is not sufficient, and it is probable that the poison increases the adsorbing power of the catalyst for the trioxide, and hence slows the reaction down. Since adsorption and surface tension are in close connection, and the absorption of the poison can hardly fail to affect the surface tension, it is claimed that there is nothing improbable in this explanation.[2]

As we have little information on catalyst poisons in the Contact Process beyond the mere fact that they act, any explanation will be received with reserve. An investigation into the poisoning of platinum in relation to the adsorption of the oxides of sulphur would probably give most interesting and useful results. Of the work which has so far been done that of Maxted on palladium bears most closely on our present object, and as it cannot be passed over by anyone seeking for an explanation of platinum poisoning, a brief account of it will be given.

Maxted[3] first of all measured the volume of hydrogen which was taken up at the ordinary temperature by palladium which had been dehydrogenated in a vacuum at 100°. On admitting hydrogen sulphide to the palladium it was rapidly absorbed and (except for a slow secondary absorption) no more was taken up after a few minutes. The hydrogen sulphide could not be removed to any great extent by exhaustion at the ordinary temperature, and the metal had lost all power of absorbing hydrogen. On heating the poisoned palladium

[1] *Chem Zeit.*, 1905, 287.
[2] Bodenstein and Fink, *loc. cit.*
[3] *J. Chem. Soc. Trans.*, 1919, **115**, 1050.

to 100° in vacuum, hydrogen was evolved and the sulphur remained in the metal.

In this way the influence of the retained sulphur on the occlusive power for hydrogen was determined, and it was found that the relation between the two was approximately linear, and that each gram-atom of sulphur rendered almost exactly 4 gram-atoms of palladium incapable of occlusion, the remainder of the metal behaving as usual. There was not sufficient evidence for the assumption that the complex is the chemical compound Pd_4S.

We have therefore for the first time a quantitative formulation of the poisoning action, so far as it affects the occlusive power of palladium. If lead is the poison the relation is the same, and in this case the poisoning not only causes the occlusion to diminish, but also the power of the palladium to catalyse the hydrogenation of oleic acid. Both occlusion and catalysing power are proportional to the amount of catalyst unaffected by the poison. The same amount of lead, however, has a greater effect on the catalysis than on the occlusion; for instance, 0·17 gram-atom of lead is required to reduce the occlusion to one half, whereas about 0·02 gram-atom is sufficient to affect the catalysis to the same extent. Occlusion by palladium is probably, therefore, not confined to the surface. Catalysis, on the other hand, appears to be a surface occurrence.[1]

This relation having been established, the poisoning action of lead, mercury, sulphur, arsenic, and zinc, on the hydrogenation of oleic acid by both platinum and palladium has been discussed. Throughout the range from the point where no poison is present to that where the activity of the catalyst disappears entirely, the relation between the amount of poison and the activity remains linear,[2] and we may infer that the occlusive power would be affected in the same way as before.

We are perhaps hardly entitled to conclude that the poisoning of platinum in the contact process may be viewed exactly in the same way; but these important results nevertheless provide us with a very excellent working hypothesis which, failing the results of any direct investigation, is more valuable than anything which has hitherto been suggested. It is difficult

[1] *J. Chem. Soc. Trans.*, 1921, 119, 1280.

[2] *J. Chem. Soc. Trans.*, 1920, 117, 1501; 1921, 119, 225.

to avoid speculation whether arsenic forms in platinum a complex similar to that given by sulphur in palladium. The investigation on these lines of the effect of arsenic (say in the form of oxide) on platinum, from the point of view of the Contact Process, would be of great interest and could hardly fail to give—what may be known but have not been revealed—quantitative data for the poisoning.

Ferric Oxide.

Ferric oxide has played a considerable part in the development of the Contact Process, and is still in commercial use in plants of the Mannheim type. Compared with platinum it is a very inactive catalyst; but this disadvantage is partly outweighed by its cheapness, which allows any desired quantity to be used without great initial expense, and to be renewed at frequent intervals.

A rough idea of the great inferiority of ferric oxide to platinum can be gained by glancing at the curve F of Fig. 13. At about 550°, when 0·5 gm. of platinum are converting 30 litres of gas per minute to the extent of 70 per cent., a very much larger amount of the oxide (there is no record of this amount) can only convert half a litre to the extent of 46 per cent. In the Mannheim plant the conversion is first partially carried out to 40 per cent. or so by means of ferric oxide and is then more or less completed by platinum. It is usual to have about 30 tons of oxide to 4 or 5 lbs. of platinum. Further details will be found in the description of this type of plant.

The formation of sulphur trioxide by the catalytic action of this substance was investigated by Lunge and Pollitt.[1] They found that the percentage conversion was not sensibly affected by changing the dilution from 2 to 12 per cent., though above this the conversion falls off. The mixture of gases to be used must be as dry as can be obtained by thorough treatment with sulphuric acid. Neglecting this precaution, the contact action not only decreases, but the mass has to be treated for a long time with the dry mixture before it recovers from the "poisoning" action of the moisture. The same effect is obtained by using oxide which has been exposed to the air and has therefore absorbed some moisture.

[1] *J. Soc. Chem. Ind.*, 1903, 22, 79.

The residue from the burning of pyrites, or ferric oxide obtained by heating hydroxide, was found to be much more efficient than that made by ignition of either of the sulphates of iron, the reason being almost certainly that the physical state of the former materials was superior. The addition of copper oxide was found to be favourable to conversion. Arsenious oxide is completely taken up and retained by the oxide at a high temperature (the best temperature appeared to be about 700°). Considerable quantities of arsenic can be absorbed in this way, and if the mass contained 2·75 per cent. of elementary arsenic it showed a contact action 60 per cent. in excess of the pure oxide. The same conclusions were found to apply to oxide containing copper. The best temperature was found to lie between 600° and 620°. Below 600° the action was very slight; above 620° it decreased until a certain point was reached and then remained constant until 750°, after which it again fell. The conclusions in regard to temperature were confirmed by Lunge and Reinhardt,[1] who obtained a maximum yield of 70 per cent. at 625°. The action was perceptible at 400°.

The question of the obtainable yield at various temperatures is a somewhat complicated one, for besides the gas reaction there is also the possibility of absorption of trioxide by the sulphate, or of the evolution of trioxide from it. On heating ferric sulphate in an atmosphere containing trioxide, trioxide will be evolved from the sulphate up to a point where its partial pressure in the gas is equal to the dissociation pressure of the sulphate. This point will be reached, assuming that all the trioxide is not removed as it forms, before all the sulphate has decomposed. It is consequently unnecessary to work at so high a temperature that the sulphate has all dissociated; one at which the partial pressure of trioxide is equal to the dissociation tension is all that is required. If the temperature falls below this point, the trioxide will be absorbed by the iron oxide. If, without altering any other condition, the concentration of dioxide passed over the catalyst is increased, the temperature must be raised also, for otherwise the increased partial pressure of trioxide would cause further combination with the catalyst.

[1] *Z. angew. Chem.*, 1904, 17, 1041.

The calculation of the optimum temperature for various gas mixtures was carried out by Keppeler and D'Ans,[1] to whose work reference has already been made. They measured the dissociation pressure of the trioxide above ferric sulphate at various temperatures by a dynamic method. Nitrogen was passed slowly over the heated oxide, removing the gaseous products of the dissociation—

$$Fe_2(SO_4)_3 \rightleftarrows Fe_2O_3 + 3SO_3 \rightleftarrows 2SO_3 + O_2,$$

so that the partial pressure of trioxide, and also the equilibrium between the three gases, could be determined. The equilibrium was found to be in good agreement with the data given by Bodenstein. The partial pressure of trioxide in double equilibrium with the other gases and with the sulphate was found to be 1 mm. at 550°, 15 mm. at 640°, and 109 mm. at 720°. From these data, by a special method involving the assumption that the partial pressure of oxygen does not change very much, the following yields and "optimum" temperatures for various gas mixtures were obtained:—

Per cent. SO_2.	2.	3.	4.	7.
Temperature . . .	629°	640°	650°	665°
Yield	72·5	...	65·0	53·2

These data may be taken to indicate the yields possible under ideal conditions. Yields in practice are never so high, for the process is not one capable of nice regulation, and ideal conditions are much more remote than in conversion by platinum.

The question of the absorption of arsenic by the oxide and its effect is one of considerable interest. Arsenic in the form of oxide is taken up very readily from hot burner-gases by pyrites cinder, and the work thrown on the purification system of the plant is in some degree lessened. But it is not thought desirable to allow too much arsenic to accumulate. In practice some of the oxide is replaced at frequent intervals, and the percentage of arsenic in it is kept down, often to 2·5 per cent. In Lunge's second paper quoted, the question of the influence of arsenic was resumed. Pyrites residues charged with arsenic were found in the best case to have about the same conversion

[1] Keppeler and D'Ans, *Z. angew. Chem.*, 1908, **21**, 532 and 577.

as pure ferric oxide, and the conclusion that arsenic has a favourable influence was confirmed by the observation that a 70 per cent. yield could be obtained at 625° from ferric arsenate. Arsenic pentoxide was found to possess strong catalytic powers even when free from iron. The most rapid action was at 675°. Copper, it may be mentioned in passing, was found in the experiments to have no influence in small amounts and an adverse one in greater quantity.

In continuation of this work, arsenic pentoxide as a catalyst was examined by Berl.[1] The substance was employed in some cases as a smooth layer on the inner surface of a glass tube, but usually in a porous and granular form, and the velocity of combination was observed from the fall in pressure of the gas mixture at constant volume. The catalytic power of the oxide at first decreases, and then acquires a constant value with an activity comparable to that of ferric or vanadium oxide. Moisture in the gases over and above that left after sulphuric acid-drying is deleterious, but the more intense drying produced by phosphorus pentoxide is also to some extent injurious.

In the Mannheim plant (*q.v.*) the ferric oxide catalyst is usually contained in tall square brick-built shafts with an entrance from the pyrites kilns at the bottom. The gas ascending is cooled in its ascent, and the temperature of the oxide varies from top to bottom of the shaft. It is certain that long contact with the catalyst is necessary to equilibrium (Haber expresses a doubt whether equilibrium has so far ever been obtained), and under these conditions of varying temperature the higher results of the various investigations described are hardly to be expected. A conversion of 40 per cent. with a burner gas of 5 to 7 per cent. SO_2 is a good one.

It is always found in practice that a contact-shaft of new oxide requires long heating to bring it into condition. The conversion obtained from it is dependent on the careful preliminary drying of the air admitted to the kilns. The conclusions of Lunge and others are thus borne out by practical experience. It is sometimes stated that overheating of a contact may cause loss of activity owing to reduction of the

[1] *Z. anorg. Chem.*, 1905, 44, 267.

mass to magnetic iron oxide, a change which was thought by Lunge to play a considerable part in the action of the catalyst. This has never been established.

Many proposals have been made to improve the action of ferric oxide as a contact substance. It has been proposed to mould the oxides of iron and copper or chromium into briquettes with clay, and to place these in the contact-shaft (B. P. 11792 of 1901). It is difficult to see what would be gained by these means, and more interest attaches to the plan of converting part of the cinders removed from the bottom of the shaft into sulphate by moistening with sulphuric acid and then replacing them at the top. This material gradually passes down the shaft and the sulphate formed is dissociated, giving rise to a finely divided oxide which is said to be more active than the cinder variety (Ger. P. 163835). The formation of briquettes of the oxide by the use of sulphuric acid has also been proposed, possibly with the idea of avoiding the dust which is so troublesome in practice.

By mixing ferric oxide with the oxide of barium or strontium, and heating in air, substances are obtained which are said to have high catalytic power. Their catalytic action is said to begin at 400° and to produce a 94 per cent. yield at 450°. It is claimed that the sensitiveness to water is not so great as in the case of ferric oxide alone (U.S. P. 1018402 of 1911).

The *Badische* Company claimed an advantage in the use of iron, copper, or chromium oxide as a carrier for platinum (B. P. 10729 of 1901). Burnt pyrites, which must be entirely free from arsenic, is sized and cleared of dust, and 145 parts are then impregnated with 30 parts of a solution of platinum chloride containing 17 gm. platinum to the litre. The resulting product can be used at once as a catalyst, or may first be heated. Such bodies are not molecular mixtures, but are formed of granules of metallic oxides covered with a layer of platinum. The catalytic action of the platinum is increased by that of the oxides, and the product acts at least as well as platinised asbestos. These contact-bodies are cheap, offer great resistance to heat and chemical action, and require no special arrangements for preventing the pressure on the contact-material from forming an impermeable mass.

Vanadium Compounds.

The possibility of utilising vanadium compounds appears to have been known fairly early in the history of the process. The Höchst works investigated vanadium oxide in their preliminary work about 1900 and found that this substance and tungsten trioxide acted about equally well, and rather better than molybdenum trioxide, their position being in a class in advance of that containing iron oxide. Küster examined a number of catalysts to estimate their relative activities,[1] and reported that vanadium pentoxide and ferric oxide were comparable in this respect, but that the former was much less sensitive than the latter to arsenic and other poisoning, as well as to mechanical influences. Access of arsenic, if continued, caused progressive poisoning of the iron,[2] but the vanadium compound retained its activity unimpaired for an apparently unlimited time. Both catalysts were sensitive to the action of water, and the best results occurred when the usual sulphuric acid drying was employed. About 85 per cent. yield was obtained at 450° with the pentoxide, and this fell suddenly to 67 per cent. on substituting phosphorus pentoxide for the sulphuric acid.

In the Höchst patent of 1901 (B. P. 8545) asbestos was impregnated by the usual means of soaking in a solution of ammonium metavanadate, drying and igniting. The material was claimed to give a conversion of 84 per cent. at 465°. Much has been hoped for from the use of this material. A catalyst insensible to arsenic poisoning would be of great value, even though capable of only moderate activity. No practical results seem to have accrued. The patent was abandoned and in 1913 fresh patents were taken out by the *Badische* Company (B. P. 23541 of 1913; 8462 of 1914). These patents prescribe the precipitation of vanadium pentoxide on an indifferent carrier, for instance pumice, ground so finely that the particles do not exceed 20 microns in diameter. The mixture can be made with or without binding material and moulded into any desired shape. The presence of alkali salts is said to be an advantage—securing the stability of the catalyst against undue increase of temperature. For example a mixture of 200 parts of

[1] *Z. anorg. Chem.*, 1904, 42, 453. [2] *Cf.*, however, pp. 115-118.

ground pumice and 14 parts of ammonium vanadate is moulded to the desired shape, heated to 300° to expel ammonia, and then at 440° in gas containing sulphur dioxide, to produce cohesion. Or a mixture of 316 parts of ammonium vanadate and 56 of caustic potash is evaporated nearly to dryness and the residue formed into granules and heated, first in sulphur dioxide and then in air. Instead of pumice, kieselguhr or permutite may be used. It is said that catalytic mass made in this way will give 96 per cent. conversion under usual conditions.

These proposals, although promising, seem to have had little result. It is possible that some difficulty is experienced from the agglomeration of the finely divided oxide at the temperature of 500° or so, which would be required. The melting-point is comparatively low (658°), and such an occurrence seems quite probable.

The next patent is that of the Conidelon Company of Antwerp (B. P. 5174 of 1913), who proposed to use iron compounds of vanadium, obtained by adding salts of iron to a solution of vanadic acid or other vanadium compound, and precipitating the iron and vanadium together. They state that, since in the manufacture of sulphur trioxide overheating sometimes occurs to 800°, the vanadium contents of the contact-mass must be kept low enough to avoid, even at such high temperatures, the formation of easily fusible compounds, which by reducing the active surface of the contact-mass obstruct the passage of the gases. The precipitation may take place on the carrier and in such solutions that the easily fusible salts formed remain dissolved. It is also advisable to employ salts which yield on precipitation, in addition to the oxides, easily volatilising compounds, in order to obviate the presence of easily fusible products in the mass. As an instance is cited the precipitation of an acidified solution of ammonium vanadate and ferrous chloride by ammonia, followed by cautious heating to remove the ammonium chloride formed.

In 1913 the Bäyer Company took out patents (B. P. 15165 of 1913) for the use of mixtures of vanadium and silver oxides. Asbestos fibre is impregnated with ammonium vanadate and then treated with silver nitrate and washed, silver meta-vanadate remaining on the fibre, preferably to the extent of 20 per cent.

of its weight. It has been seen that vanadium pentoxide gives only about 84 per cent. yield; silver or silver oxide have in themselves very little action; and the vanadates of copper, cobalt, manganese, and many other metals are said to be less active even than vanadium pentoxide. The activity of the silver compound is therefore remarkable. The conversion at 520° is said to be practically theoretical under the usual conditions. The ratio of vanadium to that of silver used is said not to affect the results within wide limits.

This appears to be a promising method of utilising vanadium, and there is reason for believing that the claims made for silver vanadate, as well as for vanadium pentoxide, are well founded, although neither substance can rival platinum in activity at moderate temperatures.

The pentoxide, however, has been the subject of further patents having for their object the preparation of the catalyst in a suitable state of subdivision. In one patent assigned to the General Chemical Company (U.S. P. 1371004 of 1921), it is proposed to impregnate disintegrated kieselguhr with ammonium, potassium or sodium vanadate. For instance kieselguhr (316 parts), the particles of which do not exceed 60 microns in diameter and are preferably smaller, is mixed with 50 parts of ammonium vanadate in solution and 56 parts of potash. The mixture is evaporated and formed into granules which are heated to 480° first in sulphur dioxide and then in air. The means of obtaining this fine division is not stated. The presence of sodium or potassium salts is said (as in the *Badische* patent quoted) to protect the catalyst against deterioration.

The Selden Company (B. P. 170022 of 1920) find that vanadium pentoxide operates more efficiently as an oxidising catalyst if it is previously heated to a temperature (at least 500°) high enough to cause it to darken in colour, sinter, and become denser and more crystalline, or even to so high a temperature (over 658°) that it fuses. The resolidified dark bluish-black crystalline mass is broken into lumps or granules and used without a support. It is possible that the principal use of this invention may lie in the oxidation of naphthalene to phthalic acid, for which the Selden Company's patents are now being worked in this country and elsewhere; but the claim

is made that the oxide prepared in this way will oxidise sulphur dioxide at 400°.

Other Catalysts.

Metals.—It is interesting to note that the catalytic power in regard to sulphur dioxide conversion of both palladium and iridium is very low in comparison with that of platinum. A comparison of the behaviour of these three metals was made by Wöhler, Foss, and Plüddemann.[1] They used, in each case, 10 gm. of catalytic mass containing 1·4 to 1·5 per cent. of the metal, and passed a mixture of 1 part of sulphur dioxide and 2·5 parts of air at the rate of 176 to 179 c.c. per minute. A few of their results may be given :—

Conversion by Iridium and Palladium.

a = actual conversion per cent. b = per cent. of possible conversion.

T°.	Possible Conversion	Platinum.		Iridium.		Palladium.	
		a.	*b*.	*a*.	*b*.	*a*.	*b*.
450	96·0	96·2	100·0	27·0	28·1	0·5	0·52
500	88·0	89·5	100·0	56·7	64·5	9·8	11·10
550	80·0	79·9	100·0	67·1	84·0	23·4	29·20
600	70·0	68·8	98·5	60·0	85·5	27·2	38·90
650	56·0	47·9	85·7	42·8	76·5	40·0	71·50
700	43·0	34·4	80·0	27·1	63·0	35·0	79·80
750	32·0	21·6	67·5	19·2	60·0	22·5	70·00

The rate of passage of the gas mixture was made less than the platinum would have been able to deal with, in accordance with the lower activities of the two metals. The figures given thus reduce the distinction in activity.

Rhodium also is inferior to platinum.[2]

The use of metallic chromium and of a number of alloys of iron has been claimed by Classen (Ger. P. 274345 of 1913). Ferrochromium, ferrovanadium, ferromolybdenum, ferrosilicon-manganese and ferrosilicon-aluminium are said to be efficient and much superior to manganese and tungsten. Molybdenum

[1] *Ber.*, 1906, **39**, 3549.

[2] Wenger-Urfer, *Ann. Chim. anal.*, 1918, **23**, 97.

iron is best prepared with 50 to 60 per cent. of molybdenum; it enables sulphur dioxide to be converted at 400° to 550°.

A statement has been made that the alloys of silver and gold with palladium or molybdenum are active enough for technical importance.[1]

Chromium Compounds.—Chromium oxide, which had been used by Wöhler and Mahla in 1852, was proposed again in 1908 (B. P. 8102). The oxide is to be rendered porous either by calcination of such a compound as ammonium bichromate or by the calcination of certain other salts such as chromium nitrate, or from the calcination of chromium hydroxide in the presence of some substance from which a gas is evolved. A carrier may be used. The temperature required was said to be 420° to 630°.

In a patent of 1916 assigned to the Ellis Foster Company (U.S. P. 1204141 of 1916), a great improvement in the manufacture of the oxide for this purpose is claimed. The activity of massive chromium oxide is hardly greater than that of oxide of iron. The flaky material made by igniting ammonium bichromate is more active, and can be made much more so by carrying out the decomposition with a mixture of the bichromate and a salt of a heavy metal such as lead or antimony. The chromium oxide is thus obtained mixed with the oxide of the heavy metal. It is found that such oxides take up sulphur dioxide; that of lead, for instance, will absorb 100 volumes of the gas, and it is believed that this possibility is a factor in producing activity. Antimony trichloride (50 parts), for instance, is heated with 85 parts of potassium bichromate until no more fumes are evolved, and, the violent reaction being over, the dark coloured, spongy product is broken up and dried first in air and then in sulphur dioxide and air. The temperature of use is 425 to 450° and the conversion 93·2 to 94·6 per cent., but as usual no reference to the amount of [illegible] required to convert a given weight of gas is included. Of the various substances which can be made in this way that formed from ammonium bichromate and stannic chloride is preferred (U.S. P. 1227044 of 1917). Ten parts of the first salt are dissolved in water and neutralised with ammonia. Asbestos is impregnated with this and then treated with 50 parts

[1] *Chem. Trade J.*, 6th January 1917.

of dissolved stannic chloride and heated to dryness. A gas mixture of 6 per cent. sulphur dioxide can be converted at 425° to the extent of 88 to 93 per cent.

A further patent of 1919 (U.S. P. 1314952 of 1919) prescribes the mixture of metallic platinum with oxides, one of which, at least, is capable of absorbing a large volume of sulphur dioxide at 450° to 540°.

Miscellaneous.—The Ellis Foster Company also proposed mixtures of selenium and tellurium, the best of which contains from 5 to 15 per cent. of the latter element. This mixture is to be dissolved in dilute nitric acid and the solution used for impregnating asbestos. Since selenium melts at 217° and tellurium at 452°, the regulation of temperature would appear to be of more than usually troublesome. No purification of the gases beyond removal of flue dust is required (U.S. P. 1103017 of 1912).

Finely divided ilmenite has been stated to be of use and to be better than artificial mixtures or iron and titanium oxides (B. P. 5079 of 1913). The ore is treated with sulphuric acid, and the porous mass obtained is heated to expel the sulphuric acid.

Cerium oxide and mixtures of rare earths have also been recommended (Ger. Ps. 142144, 149677). The oxalates obtained in the manufacture of thorium are treated with sulphuric acid and then heated to remove the acid. A porous mass results which retains its activity for a long time. No purification of the gases need be carried out. To heat the sulphates to from 700° to 1000° has been said to improve their properties.[1]

Arsenic pentoxide has already been discussed. Asbestos soaked in phosphoric acid (Fr. P. 318770), oxides of metals of the tantalum group (Fr. P. 321573), and a mixture of gypsum and ferric oxide, have all been proposed. The sulphates of iron, cobalt, nickel, copper, manganese, chromium, and uranium have all a certain action, and of these the nickel and copper salts are the most active.

[1] Böhm, *Chem. Ind.*, 1913, **36**, 120.

PART II.—THE PREPARATION AND TREATMENT OF CONTACT-MASS.

The Catalytic Capacity of Platinum.

Little remains to be added to what has already been said in general regard to the catalytic properties of platinum. The occurrence and prevention of poisoning will be treated fully in

Catalytic Capacity of Platinum.

Plant.	Material burnt in 24 hours.	Wt. of SO_2 per hour (lb.)	Wt. of Platinum (lb.).	Wt. SO_2 per hour Wt. Platinum	Per cent. Platinum in Contact-Mass.
Grillo. H.M. Factories (1 unit) . . .	9·0 tons sulphur	1680	55·0	30·5	0·31 (Av.)
Grillo. U.S. Naval Proving Ground .	2·2 „ „	390	11·8	33·1	0·20 (Av.)
Grillo. Messrs Nobels (South Africa) .	6·0 „ „	1120	24·8	45·0	0·25 (Av.)
Grillo. U.S. Govt., Nitro., W. Virginia .	...	...	...	78·0	0·20 (Av.)
Grillo. Reported U.S. Practice, (i)* . .	...	...	...	56·0-74·0	0·10-0·30
(ii)† . .	...	...	...	67·0-70·0	...
Mannheim. H.M. Factories . . .	4·5 tons pyrites	270‡	...	85·0	60 mats 24 gm. in each
Mannheim. Messrs Nobels (pre-War) .	6·0 „ „	360‡	...	102·0	80 mats 20 gm. in each
Tentelew (England) .	9·0 „ „	770	24·2	31·8	7·0-9·0
Kuietsch's Experiments, 1st Series . .	...	...	...	22·0 (conver. = 97·5 per cent.) 54·0 (conver. = 94 per cent.)	10·0

* *U.S. Dept. of Int., Bull.* 1910, **184**, 179. † *Ind. Eng. Chem.*, 1922, p. 687.
‡ Allowing 80 per cent. oxide-shaft conversion.

connection with the purification of gases. The other particular point of practical interest is the amount of platinum required to effect a given amount of conversion.

The duty of one unit weight of platinum varies considerably with the type of plant, and the method of operating it, and figures which are generally applicable cannot be given. The preceding digest gives various figures obtained from actual

practice and elsewhere. In each case the ratio of the weight of sulphur dioxide passing over the catalyst in one hour, to the weight of platinum employed, is given as closely as possible. Since the capacity of the burners is always variable, this ratio is variable also. The figures given have been chosen to represent operation at the average full capacity. No figures for percentage conversion are given, for they depend on many factors, but it is natural to expect higher conversions with the lower values of the ratio in the last column but one—an expectation which, in general, is justified by the facts. It is certain that some of the most modern and highly developed types require less platinum than is anywhere indicated in this table. A considerable reduction is undoubtedly to be effected by conversion in converters in series—an arrangement which allows, as will be seen later, a greater economy of catalytic substance than any other method.

Catalyst Carriers.

Many substances have been proposed at various times as supports for platinum and other catalysts for the Contact Process, and have been used experimentally, but only two of them have been pre-eminent in surviving the test of experience —asbestos and magnesium sulphate.

A satisfactory carrier must possess several qualifications which, taken together, are difficult to find in any one substance. It must first of all be porous and expose a very large surface in order to give full play to the diffusion of the gases to all parts of the platinum. It must be, if possible, chemically resistant to the action of sulphuric acid and the oxides of sulphur at high temperatures, and must not disintegrate if made accidentally much hotter than it is usually allowed to be. Since contact-mass has to be transported and filled into the converters, and while in them may have to sustain considerable mechanical action from the swiftly moving gas-current, the support must be fairly hard, or elastic enough to resist these strains. Lastly, since the recovery of platinum from spoilt contact-mass is always a possibility and sometimes a regular operation, it must be possible to recover the very expensive platinum with the smallest possible loss. All these

requirements are fulfilled in a high degree by the two materials mentioned.

Asbestos.—The asbestos found in commerce is of three kinds, of which the most common, used for spinning and weaving, is the long-fibred mineral chrysotile—hydrated silicate of magnesium. Of all three this is the most easily disintegrated by high temperature—on account of its high-water content—and the least resistant to acids. Even such weak acids as acetic acid act on it, and boiling for four hours with 5 per cent. hydrochloric acid decomposes it entirely. The residue has the form of the original material, but consists only of hydrated silica without any considerable tenacity or tensile strength. The formula of chrysotile is $3MgO,2SiO_2,2H_2O$, and the sensitiveness to acids is a consequence of the high ratio of base to acid—3 molecules to 2. When acted upon by hot sulphur trioxide chrysotile is more or less decomposed into magnesium sulphate and silica, but the open and fibrous structure of the material nevertheless persists in these circumstances for a very long time if it is protected from mechanical disintegration. Chrysotile is used extensively in the form of loose fibre as a carrier for platinum. It is also employed, in the form of mats of woven cord in the Mannheim Process, but in this case the mats have to be handled fairly frequently and their disintegration is a serious trouble. The main supply of chrysotile is from Canada.

Hornblende asbestos belongs to the amphibole class of minerals. It can be obtained in very long fibres, but the varieties which are fine and tenacious enough for technical application all come from the North of Italy. "Italian" asbestos is a common name. Its chemical composition is MgO,SiO_2, in which the magnesia is replaced by lime or iron to a greater or less extent. Its resistance to acids is much higher than that of any other asbestos, and this resistance is maintained even at fairly high temperatures. This variety appears not to be very common in commerce.

The blue asbestos from West Griqualand is the variety known as crocidolite, in which the magnesia of the amphibole has been mainly replaced by sodium and iron. It is very fine-fibred, but the presence of sodium makes it open to acid attack, although more resistant than chrysotile, it is not satisfactory

in this respect. Heat decomposes it rather rapidly; the ferrous silicate is oxidised and the material becomes entirely brittle. This material also has been used for Mannheim mats, with poor results.

In the matter of surface, a good variety of asbestos is superior as a support to any other available substance. It may be taken that the modern types of converter, in which the amount of platinum per unit weight of sulphur dioxide has been reduced to a minimum, all use finely divided asbestos fibre. The details of the methods of platinising were, until recently, closely-guarded trade secrets, concerning which information was withheld. It is usually necessary to tease out the platinised asbestos which has been agglomerated by immersion in the solutions used, and the labour involved in this is considerable.

It was stated by the Bäyer works at Leverkusen in 1919 that the long-fibred material used by them was good for use for twelve or fifteen years, but that the short-fibred variety would not last more than ten years. In the Tentelew and other modern plants having efficient purification, the contact-mass is expected to last about this length of time without being touched.

Asbestos is found in basic rocks. The probability of its containing chlorides, fluorides, or any form of arsenic is extremely small, so that less precaution against poisonous impurity is necessary than in the case of magnesium sulphate.

Since a greater surface is presented by a given weight of asbestos than by the same weight of any other available material, the proportion of platinum which can safely be deposited on the fibre is much higher than in the other cases. It is not unusual to employ 10 per cent. In Tentelew converters in this country from 7 to 10 per cent. has been used.

Magnesium Sulphate.—The use of magnesium sulphate, and of other inorganic salts as catalyst carriers, was developed by Schröder in connection with the *Aktiengesellschaft für Zinkindustrie (vormals W. Grillo)* at their works at Hamborn. The sulphur dioxide was obtained by the roasting of zinc ores during which numerous catalyst poisons are generated, chief among which at this works was silicon fluoride. Arsenic was present as usual.

Until 1897 the line which had been followed at Hamborn

had been the conversion of pure sulphur dioxide, obtained from the blende roasting, by pumping it, mixed with air, through dense plugs of platinised asbestos. This process was obviously out of the question for the roaster gases themselves; and it was necessary to find some means whereby, in view of the inevitable poisoning, the mass could be regenerated without too much expense. It was soon found that a number of soluble salts could be made into supports of great porosity, and it was believed that some of them, *e.g.*, magnesium sulphate, actually helped the catalysis in a way which platinum could not do. Patents were taken out in all countries about 1898 (B. P. 25158 of 1898). Sulphates or phosphates were both claimed to be practicable. The salt chosen is dissolved in water, the platinum chloride added, and the whole evaporated to dryness. Platinum equal to 0·1 per cent. of the mass was claimed to be efficient. The reduction of the platinum salt is more readily effected by the addition of sugar or other carbonaceous substance, and the mass becomes thereby more porous and adherent. A further improvement was claimed in 1901 (B. P. 10412) by which the contact-mass was made in the converter itself. A current of hot air or gas was blown through the molten mass, and a very high degree of porosity resulted. Not only this, but the caking of the mass was said to prevent portions of it being removed by the gas stream.

Magnesium sulphate crystallises from a cold solution with seven molecules of water—$MgSO_4,7H_2O$—in the form known as Epsom salts. At about 33° crystals containing only six molecules of water are deposited. The heptahydrate is orthorhombic, the other monoclinic. Several hydrates are known in addition to these. At 150° the monohydrate is formed. This is the basis of Grillo contact-mass before it is platinised. At about 200° the salt may be dehydrated entirely. From a hot solution of the salt in sulphuric acid crystals of $MgSO_4,H_2SO_4$ may be thrown down, and from a cold one $MgSO_4,3H_2SO_4$. The solubility of the salt (in grams $MgSO_4$ to 100 gm. water) is given below:—

$t°$	0	10	20	30	40	50	60	70	80	90	100	108·4
gms.	26·9	31·5	36·2	40·9	45·6	50·3	55·0	59·6	64·2	68·9	73·8	77·9

The saturated solution boils at 108·4°. The heptahydrate will

just melt in its own water of crystallisation before the solution boils.

Magnesium sulphate can fairly readily be obtained pure enough for the purpose in view. It is not unusual to specify Epsom salts answering to the B.P. specification and made from "brimstone" acid, to ensure freedom from arsenic. In each case before use, careful tests for arsenic and for chloride should be made, and it is always preferable to make a small quantity of contact-mass from it, and run a conversion test in the apparatus described at the end of this chapter.

To carry this out, 500 gm. of the sample is heated in an aluminium tray, and the process for the production of Grillo mass is gone through on this small scale in the same way as described later for the large scale. The platinisation is conducted with about 20 gm. of the mass (sized to about $\frac{3}{16}$ in.). For this amount the platinum chloride is dissolved in about 8 gm. of water, and the solution is very conveniently applied with a small glass scent spray. The mass is turned over with a spatula during the spraying. After standing for a few hours it is reduced in the gas mixture at about 350°, and conversion tests carried out.

Tests and estimations of arsenic and chloride carried out on four samples of magnesium sulphate gave the following results. The ratio of the weight of sulphur dioxide (per hour) to platinum was in each case about 30:—

Sample.	Per cent. As.	Per cent. NaCl.	t C.	Per cent. SO_2.	Per cent. Conversion.
A. (B.P.) .	Nil.	0·028	415	4·64	97·1
B. . .	0·00075-0·001	0·037	410	5·70	98·0
C. . .	0·000075	0·045	405-10	5·68	95·7
D. . .	0·00001	0·124	410	4·66	95·6

The first sample was selected, for the conversion of 97 per cent. was obtained immediately, whereas B, C, and D gave at first only 90 per cent. or less, and required heating in the gas stream to 500° to gain full activity. This test is a positive one, and should not be omitted without good cause. Cases have been known of Grillo mass failing to give more than 88 to 90 per cent. conversion for no easily assignable chemical reason.

It should be noticed that the method of reduction of the platinum is a matter of importance, for unless care is taken thoroughly to remove all the accompanying chlorine, sufficient may remain to cause poisoning and low yields. Chlorine compounds produced in this way, or originally present, are, however, removed by continuance of the heating in the gas stream.

Grillo contact-mass has many advantages, and it is probable that its future use will be by no means confined to plants of the conventional Grillo type.

The Production of Magnesium Sulphate Mass.

It is not possible to make satisfactory contact-mass by merely calcining magnesium sulphate. Such material is far too friable and its use leads to disaster. The method first to be described was used at H.M. Factories during the War, and was founded on much practical experience of the material in South Africa and elsewhere. The salts are first of all calcined in iron pans, the product is ground to a fine powder and mixed with water in the hot pan and calcined again. It is then crushed and sized.

The mounting of the pans is shown in the diagram of Fig. 16. Six pans were mounted on each furnace. It will be seen that there are dampers under each pan. By regulating these, the distribution of heat along the row could be made more or less even. In describing the process, an output of 3000 lbs. of finished mass will be taken as a basis; for this amount eighteen or twenty such pans, each measuring 4 ft. 8 in. × 3 ft. × 4 in. deep, would be required. The sequence of the operations and the quantities involved are best followed by means of Fig. 17, which represents a flow sheet of the daily production on this basis.

The First Calcination.—The usual charge for a pan is a single bag, *i.e.*, about 210 lb. This is put into the hot pan, and the melting down is assisted by stirring with wooden tools shaped like mallets with long handles. The average time required to convert the salt into a dry cake is about seven hours. When perfectly white and free from moisture the cake is detached from the pan by chisel-pointed bars about

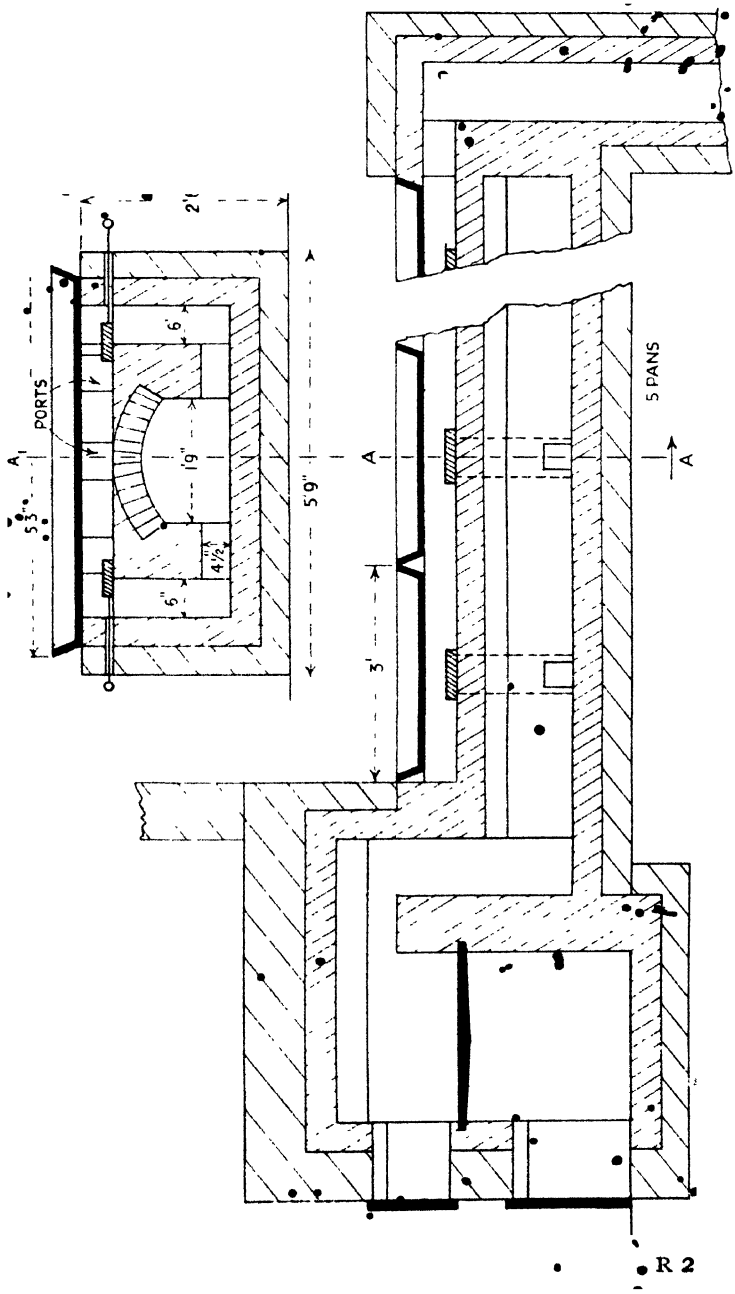


FIG. 16.—Calcining Pan-Furnace for Grillo Mass.

5 ft. 6 in. long and 1 in. diameter. As soon as the cake is cooled it is crushed, the crusher being set to give the finest possible product, and is then fed into the disintegrator and reduced to a powder which should resemble flour as closely as possible and contain the minimum amount of gritty particles. About 55 per cent. of the weight of Epsom salts is obtained as first cake, *i.e.*, about 115 lb. from a pan. The

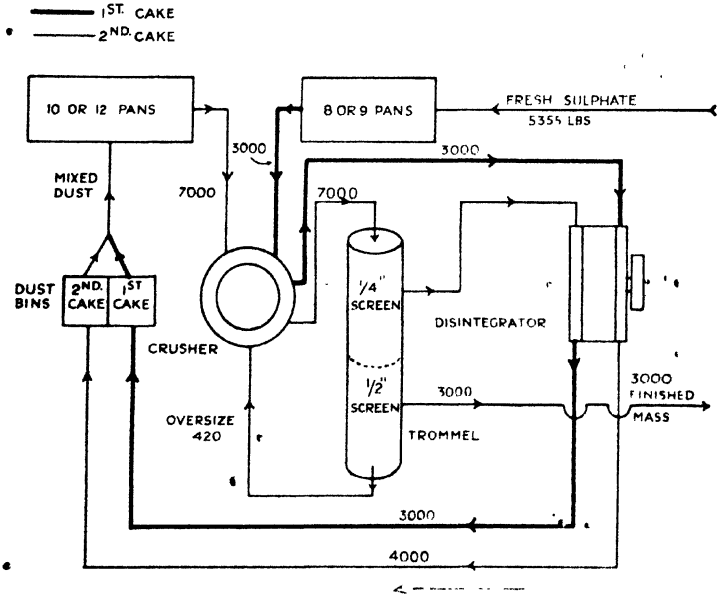


FIG. 17.—Grillo Mass Production—Flow Sheet.

moisture remaining in the cake is from 12 to 14 per cent. This corresponds almost exactly to $MgSO_4,H_2O$ (13·0 per cent.).

Second Calcination.—For this the hottest of the pans must be used. The usual plan is to employ all the pans nearest to the fires, the others being used for the first cake. Those which are to be used for this second operation should appear bright red-hot in the dark.

In the production of second cake, two kinds of material are used—dust from first calcination and dust made by grinding the fines from the crushing of the second cake previously made. First cake dust gives excellent second cake, but dust made from

second cake cannot be used alone to make satisfactory second cake again. The two kinds of dust are accordingly put into an open bin divided into two by a partition, each kind being put separately into its own part of the bin.

When a pan is charged, two buckets of the first dust and two of the second are put on to the hot pan, and water is added from a watering-can with a long spout but without a rose. The dust is thoroughly mixed with the water by means of a long handled steel garden rake 15 in. broad. About 130 lb. of dust and two and a half buckets (75 lb.) of water are added altogether, in order to obtain a mixture of the consistency of thick cream. The water evaporates rapidly during and after the mixing, and the raking is continued to assist the formation of the hard cake at the bottom, and to break up any crust that may form at the top, until there is no liquid matter left. The cake is left in the pans until it is baked absolutely dry, and, in case of the hotter pans, has become red-hot nearly all over. It is then broken out with iron rods, left to cool and crushed. The average time required for a charge is about five hours, and the weight of cake obtained is nearly equal to that of dust put in the pan.

Before crushing care must be taken that the crusher is set to give, in this case, the coarsest possible product. The crushed material is transferred by hand to the hopper of the trommel from which three sizes are obtained: (1) Finished mass $\frac{1}{2}$ in. to $\frac{1}{4}$ in; (2) fines $\frac{1}{4}$ in. and less; and (3) oversize above $\frac{1}{2}$ in. The feed to the trommel should be continuous and not intermittent, to prevent fine material passing over the finer of the two screens and passing out with the finished mass. Oversize amounting to about 6 per cent. of the total weight crushed is returned to the crusher. The fines are ground in the disintegrator as fast as they come from the screen. On a day's run the finished mass is found to be 43 to 44 per cent. of the total crushed.

A daily sample is taken by putting a handful of finished mass from each bucket weighed into a sample can. At the end of the day the contents of the can, which should amount to 60 or 70 lb., are ground in the disintegrator and the ground stuff is made into a heap and quartered in the usual way. Daily estimations of moisture are made, and the

percentage is rarely found to be below 9 or above 10. Unplatinised mass weighs about 46 lb. to the cubic foot.

The output of 3000 lb. can be obtained only by continuous work for the twenty-four hours unless there are more than twenty pans. The disintegrator should be of relatively large size as the load on it is a heavy one and, if large outputs are required, continuous feeds to both disintegrator and trommel are a great advantage. The pans are apt to bulge downwards in the places where the heat is greatest.

Magnesium sulphate mass made in this way is a hard and resistant substance. It stands transport well, especially after keeping for a few days. If storage is necessary the bins should be lined inside with ruberoid, or some other impervious lining. On a plant of this size a great deal of dust is raised from the trommel and disintegrator, which, although harmless, is irritating and a delay to work, and it has been found advisable to fit a fan by means of which this dust is withdrawn and collected in a bag for re-use.

Platinisation.—The application of the platinum to the surface of the mass is best carried out in baths of glazed earthenware, about 6 ft. × 3 ft. × 8 in. deep, and supported on brick standards about 18 in. from the ground. A rubber sheet in a wooden tray is sometimes used, but for applying such expensive material the earthenware baths are advisable for their cleanness and freedom from waste. The floor of the platinising house should be of concrete, and should drain into a sump in which scrap iron or granulated zinc is kept, to catch any platinum which may be spilled.

Before platinisation all mass is riddled carefully over ½-in. riddles to remove fine stuff which may have passed the finer screen of the trommel, or may have been produced in transport or storage. The riddled material is then weighed out into iron cans (dust-bins) 100 lb. in each. Two of these cans are emptied into each platinising bath, and the mass is spread out in an even layer by means of a wooden rake.

In 200 lb. of mass there are very nearly 180 lb. of anhydrous sulphate. The amount of platinum chloride required to give the desired percentage of platinum, reckoning on the 180 lb. of anhydrous sulphate, is then weighed out and dissolved in an earthenware jar of about 4 galls. capacity

(Avoid the use of enamelled iron. The enamel rarely resists the intensely corrosive action of the chloride.) The platinum is usually supplied in the form of chloroplatinic acid containing 40 per cent. or rather less of metallic platinum. The weight of water required to secure even distribution varies between 20 and 30 lb., but is generally about 22·5 lb. (2 galls. and 1 quart). Considerable heat is evolved during platinisation, and care should be taken that mass should not be used which has come directly from the mill and still retains heat. It has been found that more regular results are obtained where

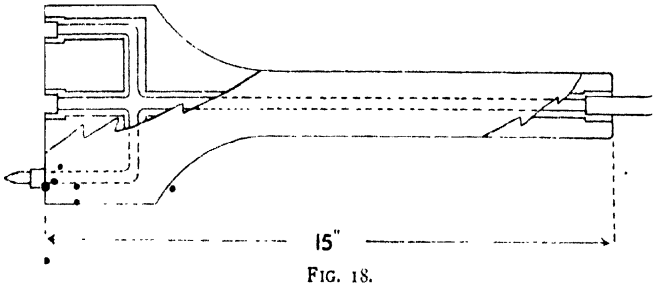


FIG. 18.

two bins are available, by putting all freshly made mass for a time into one bin and drawing for platinisation from the other.

The spray by which the solution is applied consists of four fine glass jets, connected by short lengths of rubber tube to a glass tube having four short branches and one longer one sealed on, in the form of a fork. This arrangement is enclosed in a wooden case from the end of which the jets project, and is illustrated in Fig. 18. The longer branch of the fork is connected by means of a long black rubber tube and a glass siphon to the jar containing the solution, which is placed on a shelf about 3 ft. above the level of the bath. About half of the solution is placed in the jar and spraying is begun. As soon as the surface of the mass has been covered, the surface layer is raked to one end and spraying is continued. This goes on until all the mass has been raked into a pile at one end of the bath. The pile is then turned over to expose the mass at the bottom, which so far has not been covered. By this time the first half of the solution has probably run out. The second half is then

put in and spraying is continued, the rake being driven evenly through the mass from one side to another in a regular manner until all this solution has also been used. At the finish the mass should appear wet. It should be turned over with the rake for about five minutes after spraying has finished, and allowed to remain on the trays for at least eight hours before removal to the converters.

Another method of manufacturing Grillo contact-mass, which has been used in America, consists in the combination of the baking and platinising operations. The magnesium sulphate is first treated with platinum in solution and is then baked and ground as usual. By this means an even distribution of platinum is obtained, but the metal is deposited throughout the mass, and not mainly on the surface where it is most useful. In addition, it is easy to see that unless elaborate precautions are taken the loss of platinum is likely to be a very high one, particularly from the grinding and crushing operations. This method was used in preparing the 400,000 lbs. of contact-mass which filled 100 of the 120 converters of the Old Hickory (War) plant of the U.S. Government, probably the largest contact installation ever erected. The loss in preparation and handling before insertion into the converters has been estimated at 7·5 per cent. Even allowing for this, the platinum obtained on recovery from the mass after the Armistice fell considerably short of the expected quantity.[1]

About 1000 lb. of Epsom salts are taken and the platinum in very dilute solution is sprayed on. After the solution has soaked in, the mass of crystals is thoroughly mixed and is then shovelled into the hearth of a baking furnace, a sketch of which is given in Fig. 19.[2] The furnace is so constructed that the products of combustion pass first underneath the hearth then over a bridge at the far end, and back over the hearth to the chimney. In one side three wide doors are provided through which the charge can be rabbled. A shelf about 1 ft. wide extends along the side of the furnace at the hearth level.

The hearth should be hot and the flame should be a reducing one when the charge is put in. The sills of the doors should be luted with 6 to 8 in. of dry dust to keep out

[1] *J. Ind. Eng. Chem.*, 1922, **14**, 636.

[2] *U.S. Bureau of Mines, Bull.*, 1920, **184**, 176.

excess oxygen. As a crust forms on the hearth it is broken up and the whole cake is turned over with a flat-nosed steel bar. This is continued until material corresponding to the first cake already mentioned has been formed and the product is then raked out, cooled, and ground in a pair of close-set fluted rolls, or on a grinder, care being taken to avoid dust loss. The ground material is made into a paste with water, and the solid mass which forms is roasted again in the same way, the hearth being rather hotter than before, and the product from the second roasting is crushed between rolls and sized as required.

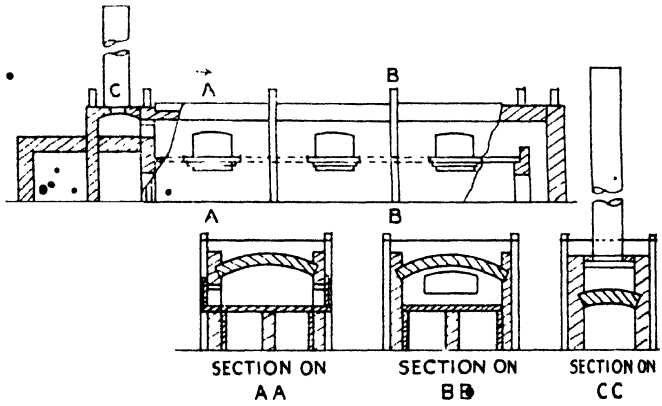


FIG. 19.—Calcining Furnace—Reverberatory.

The use of the furnace shown in the sketch is, of course, not restricted to this combination method, for contact-mass intended for subsequent platinising by the more approved procedure can be made in it, instead of in the rows of fire-heated pans illustrated in the diagram of Fig. 16.

Preliminary Treatment in the Converter.—The platinised mass is packed into the sections of the converter with great care, to secure even resistance to the passage of the cases. The method of beginning the reaction with it is an extremely simple one. The converter having been filled and closed up, the mass is slowly heated to about 350° by blowing heated air through it. Hydrochloric acid comes off accompanied by water and the mass is probably made more dry than it was before platinising. Burner-gases rather more dilute than

usual are then passed slowly in. The reaction begins at once. The charge burnt is increased slowly for some days until the plant is running normally.

Revivification and Reworking of Grillo Mass.—Grillo mass which has been poisoned by arsenic is often revivified by merely spraying with dilute aqua regia and replacing in the converter. In this way the arsenic is converted into arsenious chloride and volatilised. This has been found to work well. The operation may be carried out a number of times with the same mass, but the more often it is done the shorter becomes the period between two successive treatments. As a final operation in this case, and in any when the poisoning has been extreme, the platinum is recovered from the mass, purified, and sprayed again on to fresh mass, which may in certain circumstances be made from the recovered magnesium sulphate.

A method which has been used extensively in the United States and elsewhere is to dissolve the whole mass in aqua regia, and recover it by concentration of the solution. Here again the platinum will be throughout the mass instead of only on its surface. Sufficient water is taken to convert the anhydrous mass into a substance having the composition $MgSO_4+5H_2O$, and about 35 galls. of aqua regia to every 1000 to 1200 lb. of mass are mixed with the water. The mass is introduced carefully into the acid liquid. A violent reaction occurs, and if the liquid is kept hot, the whole of the mass goes slowly into solution. On cooling, the mixture sets to a solid. It is then put through the process for making fresh mass by the combination method which has already been described. Cane sugar is often added to help the mass to cake on baking.

The method given below[1] has been employed by the Modderfontein factory of the Nobel combine and has proved very satisfactory in practice. The recovery of platinum is not an easy matter, and unless great care is taken the losses are apt to be high. It is particularly important to beware of the possibility of the formation of colloidal platinum in hydrochloric acid solution. In this way heavy losses may be incurred,

[1] It has been published in *Technical Records of Explosives Supply*, 1921, 6, 68.

although the solutions run to waste are absolutely clear and yield no precipitate on scrap iron.

Breaking down the Contact-Mass.—A dissolving tank of about 450 galls. capacity is three-quarters filled with water, and a sieve made from a carboy crate lined with 28-in. wire gauze is lowered into the tank by means of a pulley, until half submerged in the water. This sieve retains the larger particles of iron scale, while allowing the platinum to pass through. The contact-mass is then placed in the sieve by bucketsful, and as the sulphate passes into solution, more is added until about 350 lb. are dissolved. The sieve is then lifted from the solution, which is allowed to stand for at least three days. At the end of that time the insoluble matter has fallen to the bottom of the tank, beneath the level of the tap, from which the clear liquid is drawn off into a lower tank where a further settling of three days is allowed. From this tank it is run through the tap into a lead-lined box in which it remains for two days.

Purification of Magnesium Sulphate.—The solution is then siphoned, without disturbing the lower stratum of the fluid, into a wood-lined box which is fitted with steam and air pipes. After the solution has been heated by steam to 60°, about 20 lb. of magnesium oxide is placed in a suspended 5-mesh sieve as in the case of the first dissolving tank, and the whole agitated with air until a sample of the filtered fluid gives an alkaline reaction, and shows no precipitate or colouring with hydrogen sulphide. Steam and air are then shut off and the liquid allowed to settle. After twenty-four hours the solution is usually clear, when it is decanted into an egg and blown to a feed-box in the concentrating plant. The lead lining of this box is painted with black enamel. From the box the solution is run into a series of coal-heated galvanised concentrating pans, five in number, and when a film appears on the surface of the front and hottest pan, the contents of the hot pan are siphoned into a crystallising pan in which, on cooling, Epsom salts crystallise out. The crystals are drained, and heated on a cast-iron pan, where water is driven off until a hard mass containing 13 per cent. to 16 per cent. of water is formed. This is removed and broken in a crushing machine into pieces of the requisite size. Dust and particles too small

for grading are made into a paste with more sulphate solution, and dried on the cast-iron pan in the same manner as the crystals.

Purification of the Platinum.—When the clear fluid is drawn off from the dissolving tank, it is again filled up with water and the process of solution continues until a complete shelf of mass has been broken up. The insoluble matter remaining at the bottom of the tank is washed two or three times with water to remove magnesium sulphate, and finally run through the lower faucet, which is fitted with a rubber pipe closed by a brass clip, into an earthenware crock holding about 50 galls. This crock is placed in a steam-heated water-bath and its contents treated for forty-eight hours with strong commercial hydrochloric acid at as high a temperature as possible, at the same time are agitated with air. It is then allowed to cool and settle, when the acid solution is siphoned off into a large crock of about 100 galls. in which scrap iron is constantly kept. The crude platinum mass is washed repeatedly with water, until the washings are comparatively free from dissolved iron. On account of the slight solubility of platinum black in hydrochloric acid under certain circumstances, and the possibility of free chlorine in commercial acid, in all cases where platinum, whether impure or otherwise, is treated in this way, the washings are subjected to the action of scrap iron, whereby any platinum which may be in solution is reduced by hydrogen, thrown down, and collected. The crude platinum mass is then heated with hot aqua regia, and at the same time agitated with air until the residue which remains undissolved contains no platinum. After settling and cooling the clear solution, it is siphoned into porcelain basins, while the residue is washed on a filter until free from platinic chloride. The clear solutions and washings are concentrated to a small bulk on a steam-bath, 30 c.c. of 90 per cent. sulphuric acid being added to remove lead. The concentrated liquid is then transferred to a sand-bath, where it is dried, additions of hydrochloric acid being made until the resulting dry mass is free from nitric acid. This mass is then dissolved in water, filtered and hydrochloric acid is added to the clear solution, from which the platinum is then removed by the action of scrap iron in the form of wrought-iron nails. The platinum black is collected and boiled with

strong hydrochloric acid on a sand-bath until only traces (less than 0·3 per cent.) of iron remain undissolved. In practice it is found impossible by the action of boiling concentrated acid to remove iron entirely from platinum black in this form, hence the necessity for the subsequent precipitation by ammonium chloride by means of which it is possible completely to remove the residual iron.

The platinum is accordingly washed with water until free from acid, dissolved in pure aqua regia, again evaporated to dryness and freed from nitric acid, dissolved in water acidified with hydrochloric acid and precipitated as ammonium platinichloride. The precipitate is allowed to settle, and after the supernatant liquid has been siphoned off, is transferred to a Büchner funnel where it is washed with 5 per cent. hydrochloric acid until the filtrate is free from iron. The precipitate is then dried on the sand-bath, and ignited on a fireclay crucible in an atmosphere of sulphur dioxide. The resulting pure spongy platinum is weighed and dissolved in aqua regia, and the solution freed from nitric acid as before. It is then available for the preparation of fresh contact-mass.

The iron scale and similar material, which are retained by the sieve on solution of the magnesium sulphate in the first dissolving tank, may still contain a little platinum, most of which can be removed by washing the residue in small quantities in a basin with a stream of water. The whole is agitated and the smaller particles, representing the platinum, are allowed to pass with the overflow water into one of the settling tanks, from which it may be collected on settling. The heavy portion remaining in the basin is rejected. From time to time, say after two or three shelves have been treated, any matter which may have collected in the bottoms of the lower settling tanks is washed out, and the sediment is placed in the top dissolving tank.

Separation of Platinum from Iridium.—Where a shelf has originally been impregnated with solution of platinum and iridium alloy, the presence of iridium is first seen from the difference in colour of the precipitate on adding ammonium chloride to the platinic chloride solution. Ammonium platinichloride unmixed with iridium is of a lemon yellow colour, whereas if iridium is present, the colour is a light reddish brown.

As ammonium platinichloride is less soluble in hydrochloric acid than the corresponding iridium salt, the latter may be partially removed by repeated washings with 5 per cent. hydrochloric acid, when the platinum compound approaches more nearly to its normal colour. On concentrating a sample of these washings, a cherry red substance is deposited showing a large proportion of ammonium iridium chloride.

The whole of the hydrochloric acid washings are treated with scrap iron, and the iridium is thrown down as a black precipitate which also contains platinum. To remove the last traces of iridium from the platinum salt after washing as described, it is necessary to dissolve the whole in as small a quantity of hot water as possible. The solution is evaporated to a fifth of its bulk, and on cooling 88 per cent. of the original platinum salt crystallises out, while the iridium salt, being more soluble in water, remains in solution and may be removed as iridium black on adding scrap iron.

A similar procedure was adopted in recovering the platinum from 343,000 lb. of mass from the U.S. Government plants at Old Hickory, and at Nitro, West Virginia. The dissolving tanks consisted of nitrocellulose boiling-vats, and a charge for each vat consisted of 15,000 lb. of mass and 6000 galls. of water. The mass was added to the warm water during seven to eight hours, the temperature being kept below 90°. Thorough agitation was applied. The solution was allowed to stand for twenty-four hours.

Some of the charges contained sand, which was thought to have worked its way in from the insulating layers on the preheater, and it is interesting to note that others were found to contain much magnesium oxide, and to be distinctly alkaline. The treatment which had been given to the mass, after use and before removal from the converters, however, is not specified.

In view of the large amount of mass to be dealt with and the fact that the time available was limited, the speed of the operations had to be increased whenever possible. The clear liquid was siphoned off from the top of one of the vats in which a charge had settled, whenever such siphoning was possible, and the platinum sludge at the botton was then concentrated by running the muddy liquid through the Monel metal bowl—30 in. long by 4½ in. wide—of a Sharples centrifuge. The

material which accumulated in the bowl was treated with hydrochloric acid diluted with hot water (12·5 lb. sludge, 1 gall. concentrated acid, 4 galls. water), whereby its weight was reduced by about three-fifths on account of the removal of iron and lime and other impurities, and was again centrifuged. The purified residue was then dissolved in aqua regia (20 volumes concentrated hydrochloric acid to 3 volumes nitric acid) in 6-gallon silica dishes, and after solution had been completed, as far as possible the clear liquid was siphoned away from a residue which still contained a small amount of platinum and was otherwise dealt with. From the solution so obtained the ammonium platinichloride was precipitated by adding a hot concentrated solution of ammonium chloride, or the finely powdered solid salt. Some alcohol was then added and twelve hours allowed for settling. After this the liquid was siphoned off, the precipitates from several vessels united, and three separate washings with alcohol carried out. Finally, the precipitate was dried in an iron box heated by steam coils and was then calcined in large graphite crucibles or in silica dishes.[1]

Of the 9764·5 Troy oz. of platinum presumed to have been used, 7·5 per cent. was written off for loss in preparation and handling. From the remaining 9032 oz. which should have escaped dissipation from the converters, 8812 oz. of an alloy which was considered to contain 94 per cent. of platinum. were eventually recovered. The over-all recovery would therefore appear to have been about 85 per cent. This figure should not be taken as a standard.

The Preparation of Mannheim Contact Mats.

The platinum used in the Mannheim contact ovens is deposited on mats of woven asbestos cord. These mats are laid on each other with suitable supports in the form of thick wire netting between each net. From ten to thirteen nets are built up into an "element" on an iron frame, and the element as a whole is slid into a chamber prepared for it in the contact oven. Details of the building up of the elements will be found in the description of the Mannheim plant.

[1] *J. Ind. Eng. Chem.*, 1922, **14**, 636.

The element frames are usually about 4 ft. 6 in. long by 2 ft. 3 in. wide. The mats to be used in such a frame should be about 4 ft. 10 in. × 2 ft. 6 in. to begin with, as they shrink during the preparation, and the necessary air-tight joint cannot readily be made round the edges of shrunken mats. There are from three to four strands to the inch, and any loose ends at the side should be tied back into the fabric of the net to prevent them coming unfastened.

The most important point is to obtain a quality of asbestos which will resist fairly well the process of platinising, and what is a more severe test—the disintegrating action of the hydrochloric acid washes which are used after the mats have first been baked and when they require revivification. This requirement is a difficult one to fulfil if, as has generally been the case, the ordinary Canadian asbestos is employed, for an unsuitable specimen of this material may lose 25 to 30 per cent. on washing, and may even fall entirely to pieces before the platinising is finished. But the question is not entirely a chemical one, the physical treatment which has been given to the fibres has much to do with the usefulness of the mat, and a heavy loss on washing does not necessarily imply a bad mat. The only satisfactory method of testing mats is to try them in the actual process. Crocidolite mats turn brown when given their preliminary baking and become extremely brittle, so that their treatment is rendered difficult, if not impossible.

Platinising House.—The room set apart for platinising mats should contain the following pieces of apparatus: (1) One or more enamelled iron baths large enough to take the net easily when it is lying flat, and to leave some extra space at the head and foot. A suitable size is about 5 ft. 9 in. × 2 ft. 9 in. × 12 in. deep. Each bath is fitted into a water-bath of somewhat larger size, and the water between the two vessels is heated by a steam coil. Each platinising bath should have lids which can readily be removed to allow access to either end, and a draught arrangement to carry away the steam is advisable; (2) Earthenware tanks for soaking the mats in hydrochloric acid; (3) A large wooden tank big enough to allow a whole element to be immersed at once. Sprinklers should be arranged to wash the mats on drain-boards above the bath, and arrangement

should be made for recovering any platinum passing away in these or other washings; (4) A drying-oven containing a number of grids on which the nets can be dried.

Platinising.—The methods used for platinising are the same in principle but differ somewhat in their details. Two procedures are possible. In the first the platinum is deposited evenly throughout the mat by using the minimum amount of solution; in the second excess of solution is used, and the platinum is obtained to a greater extent on the surface of the cords. The second process gives, at least at first, a somewhat more active mat, but not so enduring an article as the first, and the loss of platinum from the mat during handling and treatment is greater in the second case.

Method I.—The solutions required are: (*a*) The requisite weight of platinum chloride for one mat made up to 1 litre with distilled water; (*b*) 400 gm. of sodium formate made up also to 1 litre. The whole of (*a*) 100 c.c. of (*b*) and 600 c.c. of water are first of all mixed together in a porcelain basin of about 15 in. diameter. (The basin should be supported on sand in some other vessel to guard against breakage.) The mixture is treated with solid sodium carbonate until no further effervescence occurs, and the mat is then dipped in, corners first, the centre being held in the hand. When all the solution has been absorbed, the mat is vigorously kneaded in the dish until the distribution of solution is quite even.[1] Then the mat is wrung from the corners inwards to drive the solution toward the centre, and is then kneaded again and finally laid at the bottom of the platinising bath (the water in the jacket being at boiling-point). Care is taken to make contact between the bath and the whole underside of the mat. After about ten to fifteen minutes the underside will have begun to blacken. The mat is turned and the other side treated in the same way, and it is then rolled up and allowed to remain at the head of the bath, or in another bath, for twenty-four hours, being heated all the time. The colour after heating is light grey, and not so dark as that first developed. Washing is carried out by laying all the nets which have been platinised flat in one of the baths, and running in water almost to the top. Five washes are given, each lasting two hours—three with tap water and the

[1] The operator must wear rubber gloves.

last two with distilled water. The mats are then drained for a few minutes and dried in the oven.

Method II.—A steam jacketed bath of enamelled iron is used. The jacket should be capable of taking steam at 20 lbs. pressure. Forty litres of distilled water and about 170 gm. of good soda-ash are placed in the bath, and when the solution is boiling vigorously a mat is placed in the bath and a solution containing 450 gm. of sodium formate is added. About two-thirds of the required amount of platinic chloride, dissolved in about half a litre of water and neutralised with sodium carbonate, is then poured in slowly. The mat is kept in motion in the solution for a short time, and the cover is placed on the bath and the liquid boiled for a quarter of an hour. The mat is then turned over and the remainder of the platinic chloride added. Boiling is continued until the whole of the platinum has been deposited and the liquid has cleared completely. The mat is then removed and placed with others in another bath containing distilled water. After four or five hours the water is replaced by 10 per cent. sulphuric acid at 35° to 40°. This acid wash lasts eighteen hours, and is followed by a similar one lasting the same time, and finally by two washings with hot water, each of ten to twelve hours' duration. The mats are finally placed on racks to dry.

Preliminary Heating of Mannheim Mats.—Before use the mats are built up into contact elements, each of ten to thirteen mats. Details of this operation will be found in connection with the Mannheim plant. For the first few hours of use the new elements are extremely active, but this activity soon diminishes, and in twenty-four hours it is seriously impaired, magnesium sulphate has formed, and the asbestos has become hard and brittle. It is therefore usual to withdraw them and carry out a process of softening the asbestos and revivifying the platinum.

It is advisable to leave the new elements in the contact-oven for at least forty-eight hours. On being taken out after this period the elements are taken apart from the frames, and the whole block of mats is laid all at once on a wooden tray and immersed in the soaking tank. No attempt must be made to fold or bend the mats, and care must be taken that no part remains above water during the soaking, or it will be found to

become permanently rotten. After immersion in water for a few hours the fabric becomes softer and easier to handle. The block of mats (still on the tray) is removed from the water, placed in a bath containing 10 per cent. hydrochloric acid, and allowed to remain twelve hours or more. The acid is removed by placing the nets in a bath, covering them with water, heating nearly to boiling, and siphoning the water away. This is repeated three times, after which the mats are dried and built into elements again.

Revivification of Mannheim Mats.—When an element has been removed from the contact-oven on account of its having been poisoned, it is treated as described above, the washing being carried out with 2 to 5 per cent. hydrochloric acid. This to some extent restores the activity. The treatment can be repeated several times; but platinum is naturally lost each time in handling, and the fibre finally becomes so weak and corroded that the mats cannot properly be built up again.

After a chrysotile mat has been in use for some time the asbestos has mainly been converted into silica, the heating in presence of sulphur trioxide and the repeated washings having removed a great part of the bases. A typical composition of this kind of asbestos is SiO_2—38 per cent.; MgO—40 per cent.; FeO—10 per cent.; H_2O—12 per cent. After platinising there may be[1] SiO_2—70·5 per cent.; MgO—13·5 per cent.; FeO—4·4 per cent.; Fe_2O_3—4·7 per cent.; H_2O—6·9 per cent. A mat which had been in use for three years gave: SiO_2—78·8 per cent.; $Al_2O_3+Fe_2O_3$—8·0 per cent.; MgO—1·0 per cent.[2]

The Testing of Contact-Mass.

Before making use of contact-mass on a large scale, it is frequently necessary to make preliminary tests to ensure that the desired conversion will be attained. There is not usually need to investigate the action of the catalyst itself—the results to be expected from platinum, for instance, are fairly accurately known—but it may be necessary to examine the support which is to be used, magnesium sulphate for

[1] *T.R.E.S.*, 1921, 6, 27.

[2] Parkes, *J. Soc. Chem. Ind.* (*Trans.*), 1922, 41, 100.

instance, and to make certain that it contains no impurities which would poison the catalyst. This is best done by preparing the mass on a small scale and observing its power of catalysis under conditions which as nearly as possible approach those of technical work.

We therefore require a conversion apparatus constructed on a laboratory scale in which the temperature, concentration, and rate of flow of gas mixture can be regulated at will. Various forms of apparatus designed for this purpose are described in the literature of the subject and are more or less elaborate. Küster[1] devised a special gasometer in which mixtures of sulphur dioxide and air could be stored, but for most purposes it is more convenient to mix two regulated streams of gas as required, if the gas mixtures required cannot be obtained from the plant.

The arrangement of apparatus shown in the diagram of Fig. 20 has been found very convenient in use. It is readily constructed and involves no article which is not to be found in a fairly well-equipped laboratory. In order to produce a stream of gas consisting of sulphur dioxide and air in the proportion required, use is made of the device of forcing each gas through a glass jet in such a way that the fall of pressure on passing the jet can be maintained at any given value.

Air from the compressed air supply, and sulphur dioxide from a siphon of the liquefied gas, are passed through simple pressure regulators, by means of which the pressure of each gas can be kept constant within 1 mm. of water. The air passing the regulator is dried by passing through a drying tower and a U-tube, both containing suitable material saturated with 98 per cent sulphuric acid. The sulphur dioxide requires no drying.

Each gas is then passed through a jet made of drawn-out glass tubing. The fall of pressure due to the passage of either gas through its jet can be read on a gauge containing sulphuric acid and can be maintained at any value desired by adjusting the pressure regulator. In this way, after the proper jets have been selected by preliminary tests, it is quite easy to maintain a stream of gas containing from 3 to 8 per

[1] *Z. anorg. Chem.*, 1904, **42**, 453.

cent. of sulphur dioxide without important variation in composition, for many hours. It is advisable to have several jets

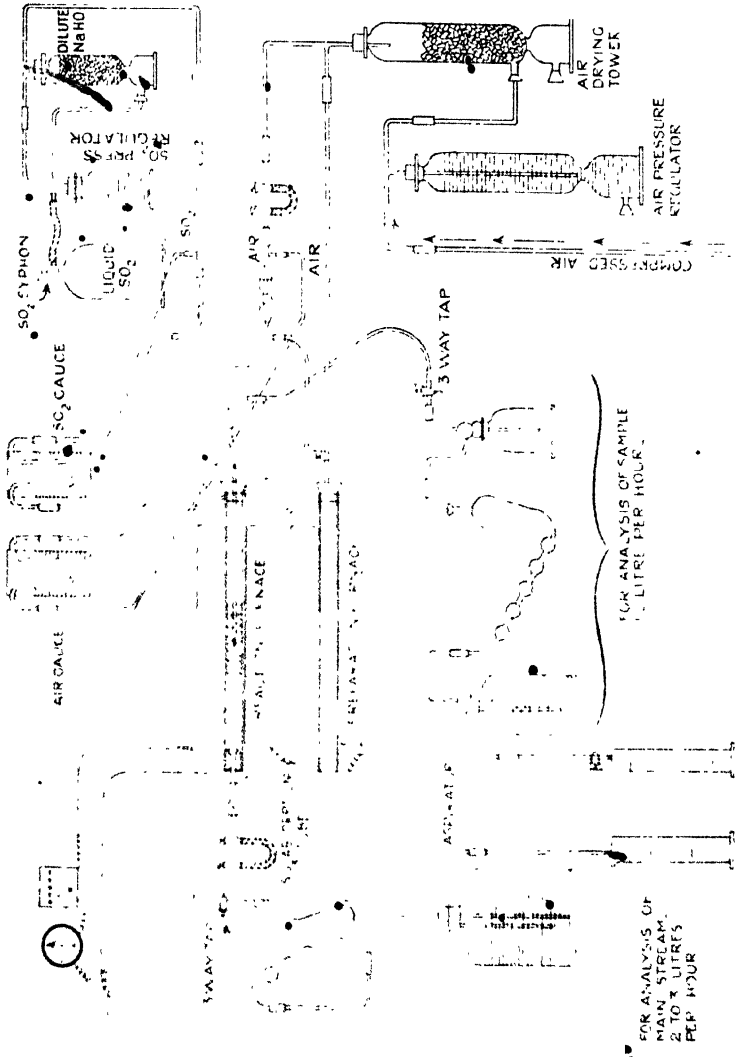


FIG. 20.—Laboratory Apparatus for carrying out Conversion Tests.

for each stream if the rate of flow is to be varied considerably, and the jets should be secured from the access of dust and moisture by inserting a small plug of cotton-wool in the wider part of each.

The streams of gas issuing from the jets meet as shown in the drawing, and are mixed by passage through a cotton-wool plug inserted at the point of meeting. During a test a sample is drawn off through a branch tube, and, by means of an aspirator, bubbled through iodine solution in a wash bottle and a bubbler.

The main stream passes through the contact tube of Jena glass. The further end of this tube can be joined to the rest of the apparatus by means of a plaster of Paris joint. Next in order is a U-tube filled with glass balls wetted with 98 per cent. sulphuric acid to absorb the sulphur trioxide. The gas then passes through a bubbler containing iodine solution, and finally into an aspirator constructed so that it exerts practically the same suction no matter how much water is run from it, and consequently disturbs the working of the jets as little as possible.

The volumes of air in the main stream and in the sample are obtained by measuring the water which runs from the two aspirators during a test. The corresponding volumes of sulphur dioxide are deduced by titrating the unreduced iodine in the bubblers.

The internal diameter of the reaction tube is measured, and a given weight of contact-mass is packed in between loose plugs of purified asbestos. A test can be carried through in about an hour, when once a steady state has been reached. The second furnace shown in the diagram, although not necessary, is useful to allow of preliminary heating of one specimen of contact-mass while tests are being run on another.

Instead of the standardised jets convenient use can be made of the gas volume-counters described by Beckett.[1]

In using an apparatus of this kind, with a comparatively short furnace and no special shape of reaction tube, it should always be borne in mind that conversion at any given temperature nearly always appears more favourable than it actually is. This results from the variation in temperature along the tube. For further remarks on this point, the account of Bodenstein's work in Chapter III. may be consulted.

[1] *J. Soc. Chem. Ind.*, 1917, 36, 1

CHAPTER V

CONVERTERS AND CONVERSION SYSTEMS

In the account which has been given of the historical development of the Contact Process, it has been made clear that each of the earlier plants contained some kind of retort in which the contact material could be heated. In this way the contact-mass was made hot enough to initiate the reaction, and, if necessary, heat could be supplied to keep it at the working temperature during operation. That this temperature must be kept within definite limits was recognised at a comparatively early date. A patent was granted to Lunge in 1888, in which it was stated that "the temperature in that part of the apparatus where the combination of SO_2 and O_2 takes place must be carefully regulated, and must be neither too high nor too low (preferably at or below a dull red heat)" (B. P. 3166 of 1888). That the reaction was a strongly exothermic one, capable of producing sufficient heat to hinder its own progress, was not fully realised by the earlier workers, although the fact seems a very evident one. It is probable that their apparatus was in most cases so small, and the rate of gas-transfer so low, that the evolution of heat was masked by the effect of radiation. The years 1898 and 1899 were marked by the publication, in patent applications, of the means by which the heat of reaction could be controlled in large converters. The *Badische* patents for cooling the converters by air or by the incoming unconverted gas were granted in 1898 (B. Ps. 15947, 15949, of 1898), as was that of the Höchst works for heating the gases to the temperature required for reaction, by means of the issuing converter gas (B. P. 6057 of 1898). The Höchst patent for regulating the temperature of the mass by the admixture of cold unconverted gas belonged to the following year (B. P. 285 of 1899).

The thermal data in connection with the reaction are set out, so far as they are known, in the table at the end of this chapter. By their means one can calculate, at least in an approximate way, the heat effect due to any given amount of conversion. If the gases are prevented by complete insulation from radiating heat away, the total possible heat of combination will not be given out, for the higher the temperature rises the greater is the proportion of sulphur dioxide which remains uncombined. Taking gas-mixtures resulting from the burning of sulphur of, say, 5 to 7 per cent., and assuming suitable inlet temperatures, it is interesting to find the temperatures which would be reached, and the ensuing conversions, supposing that no loss of heat occurs by radiation or conduction. This can be done with fair approximation if we select points on curves (1) and (2) of Fig. 11 (by trial or error) such that in each case the indicated conversion would produce the indicated temperature.[1] The results are tabulated below,

Per Cent. SO_2.	Inlet Temperature. Degrees.	Rise of Temperature. Degrees.	Maximum Temperature attained. Degrees.	Maximum per Cent. Conversion.
5	350	142	492	96
5	375	139	514	94
5	400	136	536	91
7	350	184	534	90
7	375	178	553	87
7	400	171	571	84
10	350	231	586	78
10	375	222	597	75

a 10 per cent. gas mixture being included. (The necessary specific heats are given in the list of data at the end of the chapter.) The specific heat of the gas mixture before and after conversion can be taken to be very nearly the same.

The figures in the last two columns make very evident the great dependence of the final result on the concentration of the

[1] A direct method can also be used. On Fig. 11, for each gas mixture, mark two points representing assumed conversions and the respective temperatures which would result. Through each pair of points draw a straight line which cuts the appropriate curve in a point representing the highest attainable temperature and conversion.

gas mixture and are borne out in practice where with rising concentration, the maintenance of the mass at a suitable temperature becomes more and more difficult in a converter of a simple type.

The converters which have been and are now used are of many and various types. To provide means for removing the "injurious" heat of reaction is not the only requisite (indeed this can be done without any special means beyond ordinary radiation). It is necessary so to arrange the contact-mass that the least possible quantity is required, and generally, although not always, to recover as much as possible of the heat which passes away in the converted gases, and to use it to increase the heat of the entering gases to the amount required for their reaction. Later developments accomplish the process of conversion in stages, two converters being employed in series. It will therefore be convenient to describe (1) Converters without internal heat-regeneration; (2) Converters with internal regeneration; (3) Conversion in dual converters in series.

1. Converters without Internal Regeneration.

One of the converters described in the *Badische* patents of 1898 is illustrated in Fig. 21. It consisted of a series of tubes which could be heated by gas flames. When conversion had begun and the heat of reaction was being given out, the flames could be turned down and cold air allowed to circulate upwards from *n* to L, cooling the tubes in its progress.

The earliest pattern of Grillo converter consisted of a vertical cylinder inside which were arranged several layers of magnesium sulphate contact-mass on perforated iron shelves, considerable air spaces being left between the layers. The converter was not heated but merely protected against excessive radiation, and the gases were brought to the temperature of incipient reaction by passage through tubular reheaters. In such an apparatus it is said that there is a tendency for the gases to pass most rapidly down the centre, and more slowly at the sides. In addition the cooling is more rapid at the sides, so that the conversion does not go on uniformly throughout the layer of mass. This difficulty was met in a Grillo patent (B. P. 17034 of 1900) by arranging several contact-

vessels side by side and connecting them by pipes alternately above and below the mass. The gas was thoroughly mixed by passage through the connecting pipes. A common means of effecting the same result, in cylindrical converters containing horizontal shelves, is to place a circular baffle-plate below the grid on which the mass rests.

Converters of this simple type are still in use, without any baffle-plates, and are found to be satisfactory in many respects.

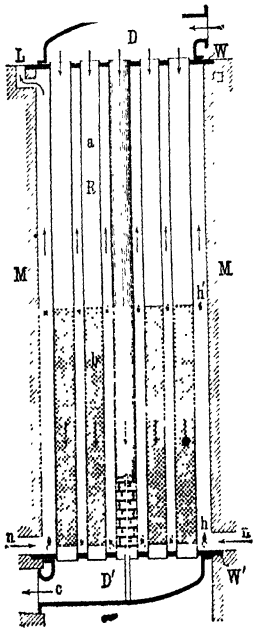


FIG. 21.

It is usual to cool the gas, issuing at about 430°, in a regenerative way, but to attempt to recover the heat lost by radiation from the converter is not always considered so important. Fig. 22 shows an example. The usual number of layers of mass is five, but four are sometimes found, and the following list of temperatures in a five-layer converter has been recorded from American practice. Inlet 385°; leaving layer (1), 540° to 560°; (2) 520°; (3) 500°; (4) 450°; (5) 385°. Of a total conversion of 96 per cent. the first layer accomplished 60 per cent.[1] For a four-layer converter an entering temperature of 400°, and layer exit temperatures of (1) 520; (2) 500; (3) 470; (4) 440, are not unusual.

The converter of Fig. 22 often consists, in American practice, of a cast-iron shell about 6 ft. in diameter and 10 to 12 ft. high, with flanged gas inlets at the base and in the cover. Ribs cast round the inside of the shell serve as supports for the cast-iron grids on which the contact-mass is placed. These shelves are spaced from 18 in. to 2 ft. apart, and the number of shelves is generally five, each carrying about 1500 lb. of mass. The coarsest material is placed first on the grids, the finest being at the top. There are usually two converters of this size on each unit, arranged in parallel.

[1] Zeisberg, *Trans. Amer. Electrochem. Soc.*, 1919, 193.

with a total capacity of 14 to 16 tons of sulphur trioxide a day, but some designers prefer smaller vessels and use four to a unit, each 5 ft. in diameter.[1]

The controlling factor in this case is the radiation from the sides of the vessel, which can be adjusted by varying the amount and position of the lagging. It has been proposed to make the converter with fins on the outside to render the radiation more readily controllable (U.S. P. 857389). To compel the gas current to spread equally through the layer of mass the device may be adopted of placing fine contact-mass at the centre of the layer, and coarser mass concentrically round it, the coarsest material being at the periphery. The layer is divided into annular zones for this purpose by open-ended sheet-iron cylinders (Ger. P. 18077).

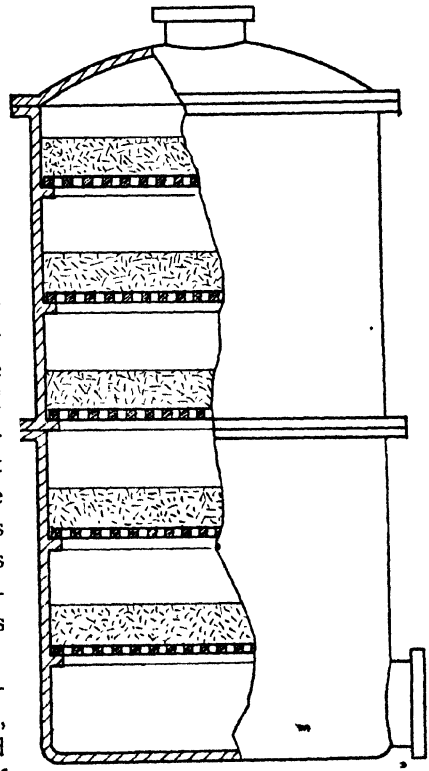


FIG. 22.—Grillo Converter—Old Pattern.

Plants were in operation quite recently which, although they possessed modern arrangements of their purifying systems, still retained this elementary type of converter. In spite of its being a not very efficient utiliser of platinum and of possessing no means of recovering a large part of the heat of conversion, it has the merit of simplicity of construction and freedom from leakage, qualities in which more complex types are often lacking.

To facilitate dealing separately with any particular layer

[1] *U.S. Dept. of Int., Bull.* 184, 173.

of contact-mass, it has been proposed to build the converter in sections placed one on the other. Each section could then be replaced by another as required (Stone, U.S. P. 71186 of 1902).

An unusual proposal to absorb the heat of reaction is that made by Blackmore (Blackmore, B. P. 27907, of 1904), to carry out the combination in the same time and place with an endothermic reaction so that the total heat liberated is zero or very small. As an instance the reactions expressed by the equation $3SO_2+2NO_2+CO_2 \rightarrow CO+3SO_3+2NO$ are, as a whole, endothermic. The patent has forty-one claims in regard to this and similar speculations.

2. Converters with Internal Regeneration.

In Fig. 23 is represented a more developed form of the converter described in the *Badische* patents. The converter body, S S, was surrounded by a brick casing so that the whole vessel could be heated to the temperature of reaction by the flames *h*, *h'*, the products of combustion escaping at L. The burner-gas passed first through the heat regulator G then through the valves V V' into chambers A and A', which supplied the whole circumference of S with gas as well as the radial pipes B B'. These were provided with holes varying in size so that the gas was uniformly distributed throughout their length. To lead the gas as near as possible to the contact tubes a number of diaphragms C were provided, forcing the stream to travel close to the pipes. The gas was thoroughly mixed before entering these pipes *via* O and F, by means of the baffle-plates in the chamber N. Thermometers placed at D and D' enabled the velocity and temperature to be regulated. Additional cooling could be obtained if required by admitting cold burner-gas through V'' and J.

Special methods were described for arranging the contact-mass. Loose platinised asbestos is apt to become compressed by the gas stream. By means of the arrangement shown in Fig. 24 the mass was placed in the tube in short independent sections, and the pressure required to force the gas through it was minimised. The mass was spread on perforated circular plates *c*, *c''* *c'''* strung round a central spindle *a* (Fig. 24 (*a*)) and separated either by short lengths of pipe, or as in (*b*) by

pins attached to the under surface of the plates. In this way the resistance to the passage of the gas was diminished and consequently the pressure required was less. Every pipe could be made to offer the same pressure and the distribution of gas in the pipes thereby made uniform (B. Ps. 15950 of 1898; 6828, 10729, 12781 of 1901). A more usual and later development of this method of separating the mass in the pipes is to dispense with the central rod and to fit each plate with a single pin which fits into a hole in the centre of the next plate.

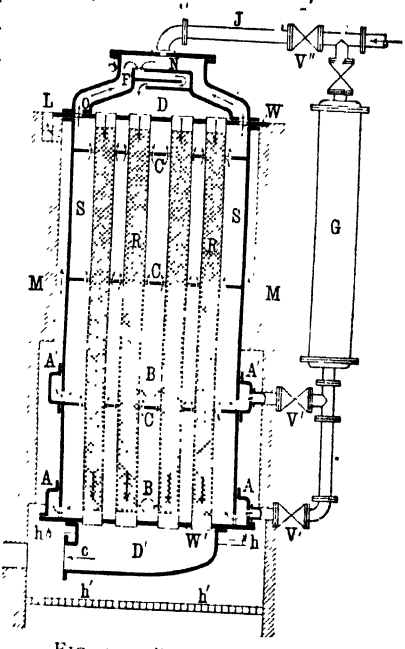


FIG. 23.—*Badische* Converter.

In all tubular converters the filling of the contact-mass into the tubes takes time and labour, and this is often said to be one of the defects of this type; but since with efficient purification the life of the mass is ten years or more, and is limited only by the gradual disintegration of the asbestos,

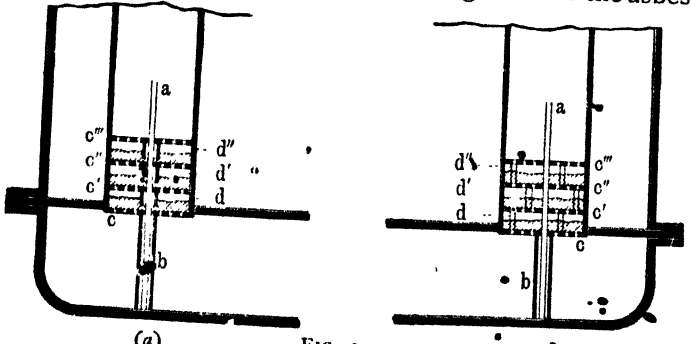


FIG. 24.

the objection has only moderate weight. The Badische type of apparatus is said to be apt to develop internal leaks.

The Tentelew converter in very general use is also a tubular apparatus, but the method of heating up the inlet gases to the

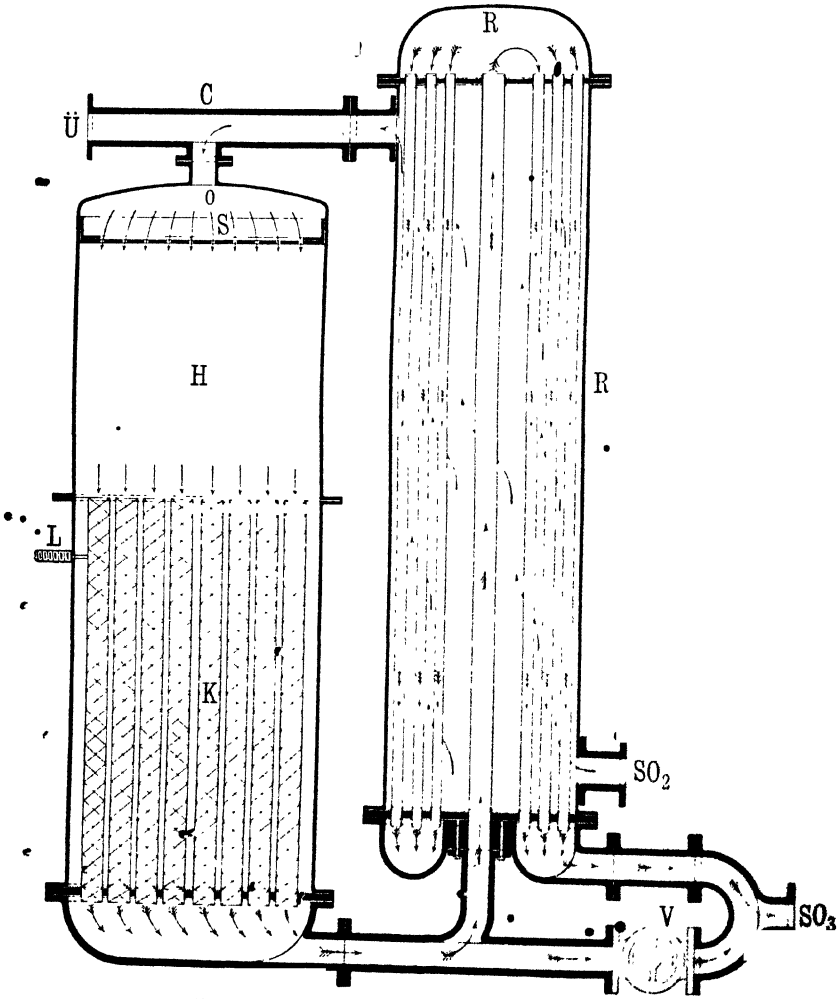


FIG. 25.—Tentelew Converter and Heat Exchanger.

temperature of reaction is quite different from that of any other type. The tubes are set in a heavy tube plate at their lower ends, but their upper ends are free. The upper end of the converter forms a free gas-space, in which the downward

velocity of the entering gas is reduced to a very low value. There is therefore opportunity for the hot tubes to impart heat to the incoming gases by convection and to some extent by radiation. This is shown in Fig. 25, which represents the converter coupled to the heat exchanger with which it usually works, as shown in the first patent (B. P. 11969 of 1902). The gas enters at C and passes through a distributing plate S, which often supports filtering material to catch dust, and then into the equalising space H, downwards through the tubes K containing the mass, and out to the heat exchanger. In practice with this converter, gas may enter from the "regulator" at 220°, be heated to 380° by passing through the equalising space to the openings of the tubes, attain 470° some distance down the tubes, and leave the converter at 430°. The platinised asbestos, containing from 7 to 10 per cent. of platinum, is packed into the tubes between perforated discs of malleable cast-iron with spaces of an inch or more between, each disc resting on a central stud projecting upwards from the one below.

The Tentelew Company in later patents (B. Ps. 20952 of 1904; 23419 of 1904) recognised that in the converter which has just been mentioned, the greatest development of heat occurred in the upper portions of the contact-tubes, comparatively little taking place at the lower ends, and proposed a division of the contact-mass into two separate portions to take advantage of this fact, and to secure more uniform temperature in the second half. The converters of this design have not come into general use. The principal portion of the contact-mass is placed on a sieve plate forming the bottom of an equalising chamber of much greater diameter than the rest of the converter, as may be seen in Fig. 26. The remainder of the contact-mass is placed in the narrower tube below this. The upper layer of contact-mass presents a large surface and can dissipate a great deal of heat into the equalising space. There are here no ends of pipes to assist this dissipation and their place is supplied by square hollow pyramids M which stand in close contact with the sieve plate. Fig. 27 shows one of these pyramids more clearly. The incoming gas, after preheating in the regulator shown in Fig. 25 and passing down through the equalising space, is said to be converted in the

upper layer to the extent of 90 or 95 per cent. Only little heat is consequently developed in the lower section of the catalyst. This section is not an assemblage of tubes, and

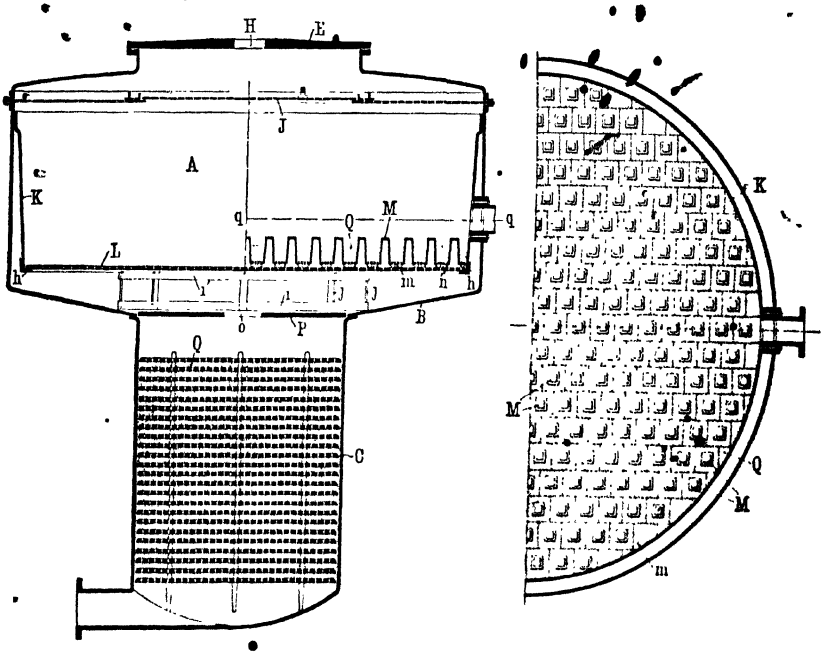


FIG 26.

since the cross section of the upper layer is greater than in the other type, the power required to propel the gas is much less than before.

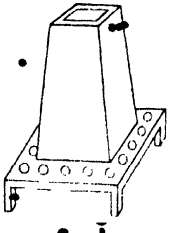


FIG. 27.

Further improvements lay in providing for a "dead" layer of gas between inner and outer vessels of the converter, and in making all parts of the apparatus more readily accessible.

The sieve L, rests on a flange *h* which is also supported from below by the rings *i*, *i*, and the pillars *j* (Fig. 26). On the sieve L is placed another sieve, composed of a number of perforated square plates *m*, *m*, each of them surmounted by the pyramids M. The principal portion of the platinised asbestos is spread on the plates *m*, *m*, in a layer reaching nearly to the

top of the cones M, M. If the apparatus is to be stopped for replacing the contact-mass entirely or partially, the top plate E is removed, then the sieve-plate J, and then any one of the plates *m*, *n* can be taken out without disturbing the others. The pyramids M, M, abstract heat not only from the contact-mass Q, but also from the plate L, and convey it by convection (radiation into the gas seems hardly likely to account for much heat transference) into the descending gas current. Plate L is made in pieces and can be taken out separately. By providing a conical empty space round the chamber A a stagnating layer of gas round K is created, which assists the heat insulation of the apparatus considerably.

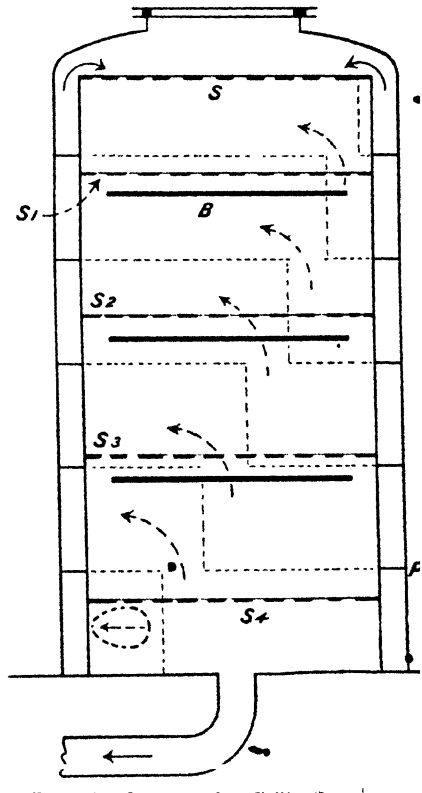


FIG. 28.—Regenerative Grillo Converter.

A converter which has been widely used is that consisting of an upright cylinder with grids inside to support the contact-mass and fitted with a jacket through which the incoming gases are circulated on their way to the mass. This is the converter of Fig. 22, with the addition of a cooling and regenerating device. The arrangement of the parts is shown in the diagram of Fig. 28. The gas enters tangentially into the space between the two cylinders at the bottom (in case of Fig. 28 it is shown entering at the back) and by means of baffle-plates P, is caused to pass almost round the converter and then upwards into the space between the next two baffle-plates, and so on until it reaches the top of the inner cylinder, having passed round this five times on its way. It then passes through an iron grid-plate S and into

the first layer of mass, which is supported on the perforated plate S_1. Issuing from this layer the gas is mixed and brought closely into contact with the inner wall by the baffle-plate B. In this way the gas passes through four layers of mass in turn and finally issues at the bottom. The whole vessel is built into a brick casing and thoroughly lagged.

This converter was used in the Grillo plants of the Department of Explosives Supply during the War and was found to be very satisfactory during the whole of the time those plants were in operation. About 2250 lbs. of anhydrous mass was used on each shelf, and the converters of a unit had a total capacity of 20 to 25 tons of trioxide in twenty-four hours. Further details of the construction and methods of filling and working will be found in the description of this plant which is given in a later chapter. When the full amount of 5 per cent. gas was being dealt with, the temperature of the entering gas was about 320°. This rose to 360° to 370° during the passage through the jacket, and the best conversion (96 per cent. or so) was obtained when the temperatures of the pyrometers immediately above the four layers were nearly the following: No. 1, 360 to 370; No. 2, 450; No. 3, 460; No. 4, 440. Under these conditions the first layer accomplished about 30 per cent. of the work conversion. By raising the inlet temperature to such an extent that the gas leaving the first layer was heated by conversion to 500° or 510°, the first layer became capable of a much greater share of the work, 60 or even 70 per cent. This is in accordance with what has already been said in relation to the dependence of the velocity of reaction on temperature.

This type of apparatus has a fairly high thermal efficiency when combined with an external heat exchanger. It is not structurally very simple, and has been found in some cases to develop leaks on extended use which, on account of the involved relation of the parts, cannot readily be repaired. For the same reason nothing can be done to influence the action of any separate layer. If, for instance, the inlet temperature is raised as mentioned above, the conversion in the first layer is greatly increased, but the other layers thereby become so hot that the total conversion falls considerably—under these conditions, probably to about 92 per cent. In

the same way it was not found possible to make economical use of a more concentrated gas than about 5 per cent., and, as will be seen later, the possibility of running regeneratively, *i.e.*, with no heat beyond that of the reaction, was barred out in these circumstances.

What is required, therefore, in all converters which consist of separate sections, is some ready means of regulating the temperature of an individual section, without disturbing the others. If this can be done, one or more may be worked at a comparatively high temperature, at which, although the maximum attainable *percentage* conversion may be somewhat lower, the *amount* of conversion will be greatly increased. In this way part of the platinum will be more fully utilised and the remainder can be reduced in amount, and—maintained at the lower temperature consistent with complete conversion—will still be able to deal with the work, which the first section has left undone, for the increased activity of the first half of the converter means a reduction of the load on the second. For economy of yield, or increase of output, whichever may be the object, two conditions are required: (1) High temperature to convert as *much* as possible; (2) lower temperature to convert as *completely* as possible. It is clear that independent sections of contact-mass fulfil these conditions best. The sections are usually more or less thermally dependent, and of the required conditions each to some extent defeats the other.

A mode of construction by which these principles can evidently be put into operation is that of the patent taken out in 1914 and assigned to the General Chemical Company (Wolff, U.S. P. 1099530). A *considerable* number of contact and heat exchanging compartments are placed over one another and directly connected. Fig. 29 shows this in diagrammatic form. The gas enters at the bottom, and, assuming both valves to be shut, passes through the two heat exchangers in succession and over the top of the internal converter into the contact-mass, down through this and through the insides of the heat exchanging tubes. By adjustment of the two valves, the extent to which the gases are cooled in their passage from one layer to another can be controlled, and the temperature of each separate contact-section can be regulated. The freedom of the

apparatus from the large amount of external piping, which would be required for control of the sections as structurally independent units, is mentioned as an advantage.

A modification of the jacketed converter which allows of controlling the extent of the preheating of the entering gases

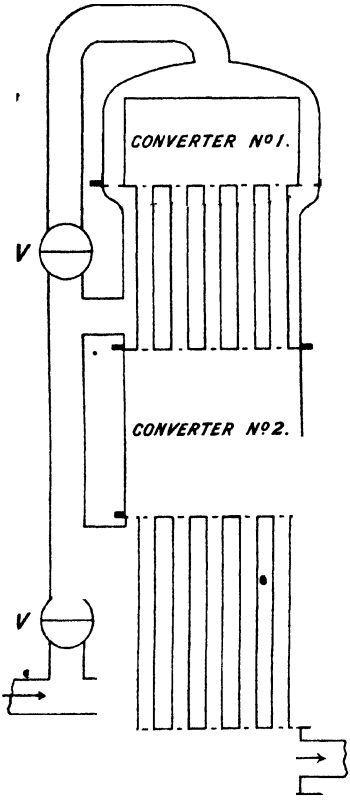


FIG. 29.

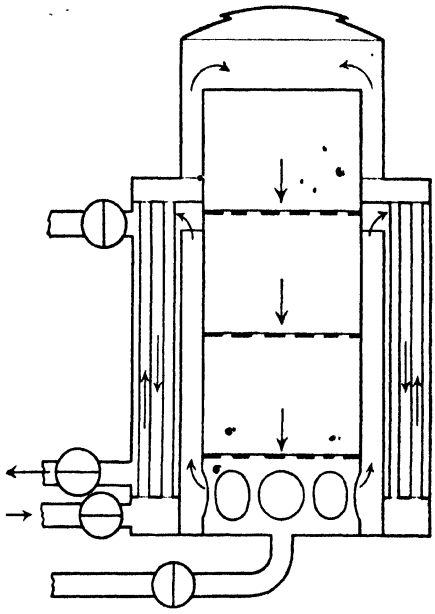


FIG. 30.

and also, it is claimed, the amount of cooling of any particular section of contact-mass, is that outlined in Fig. 30 (Parodi-Delfino, B. P. 113017 of 1917). The incoming gas passes through the tubes of a heat exchanger which is annular in plan and surrounds the converter. The converted gas passes wholly or partially over the outside of the tubes according to the adjustment of valves of three separate exit pipes. The actual jacket to the converter is formed by the gases of reaction,

which are streaming upwards from the circular openings in the inner case more or less rapidly. This jacket, however, extends only to two layers of the three shown. In the case of the first, it is replaced by the preheated gases which have just issued from the heat-exchanging tubes. The design seems rather complex.

A recent novel proposal (Audianne, B. P. 169264 of 1920) does not aim at sectional control, but is calculated to secure, in the Grillo contact-mass, evenness of temperature and gas-distribution throughout. The converter is a cylindrical chamber with a conical bottom. The gas enters this chamber, after preheating, and then passes up a large number of pipes each of which has a helical stopper fitted into its lower end. The stoppers are indicated by h, h_1, h_2, in the diagram of Fig. 31. On account of the resistance the stoppers offer, the gas passes to the same extent up each tube, with a swirling motion, and issues from their open upper ends. The contact-mass is packed into the space between the tubes. The gas passes downwards through the mass and through the two grid-plates P and P_1 on which the mass rests, and finally through circular orifices into an annular collecting channel in communication with the exit pipe. The close proximity of the tubes of colder gas to all parts of the mass secures an even distribution of temperature. The replacement of contact-mass would appear to offer some difficulty.

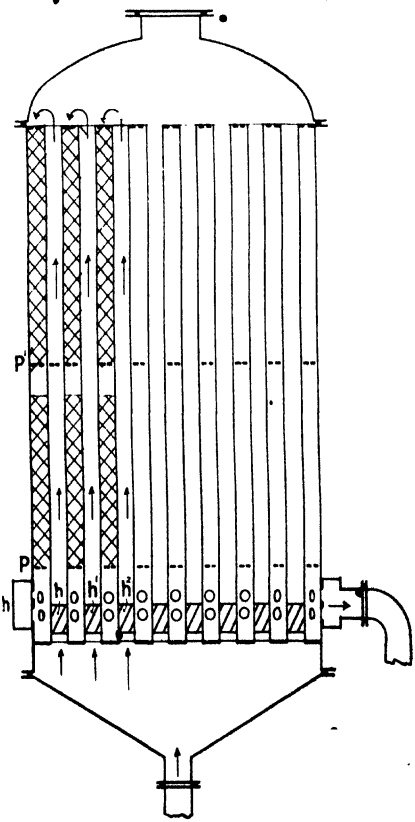


FIG. 31.

3. Conversion in Dual Converters in Series.

The advantages which are secured by dividing the contact-mass into two (or more) sections which are thermally independent have been indicated in the foregoing paragraphs. It has already been noticed that the reaction is increased in velocity forty times or more by increasing the temperature from 400° to 500°. This thermal independence of the sections is best obtained by using more than one converter, and working one at a high temperature suited for rapid action and the other at a low one to complete the conversion. This procedure appears to have been first realised by the Höchst works and

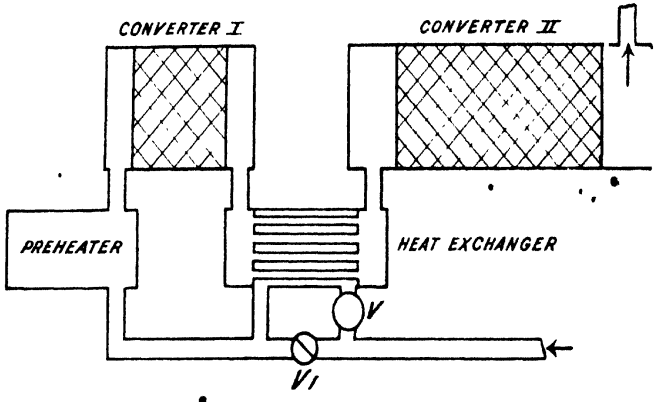


Fig. 32.

described in their patent of 1901 (B. P. 1385). A further patent of 1904 (Kaufmann, B. P. 7074) recommends the arrangement shown in the diagram of Fig. 32. After reaction at a high temperature the gas passes through a heat exchanger and, being then suitably cooled, is passed through the second converter. A similar claim, apparently by the same firm (Le Blanc and Kraus, U.S. P. 726076 of 1903), states that 75 per cent. of the conversion is accomplished in the first stage, at a temperature of 530°. The products of the reaction are then cooled by the admixture of gas which has no influence on the reaction, or in pipes, and the conversion is completed at 430°.

This idea is also the subject of the Herreshof patents (U.S. Ps. 719332, 719333 of 1903), which have been worked extensively by the General Chemical Company. The double converter appears to be typical of a number of plants in the

United States which work on this or on the Herreshof-Badische system, and it is said to result in a greatly diminished requirement of platinum. In some cases, the first converter is the larger, but contains the weaker contact-mass; the second converter is smaller and although containing richer mass, holds on the aggregate less platinum than the first.

In a later patent taken out by Knietsch (U.S. P. 809450) it is stated that this procedure may be carried out in several stages, but that two will in general be found sufficient. Working

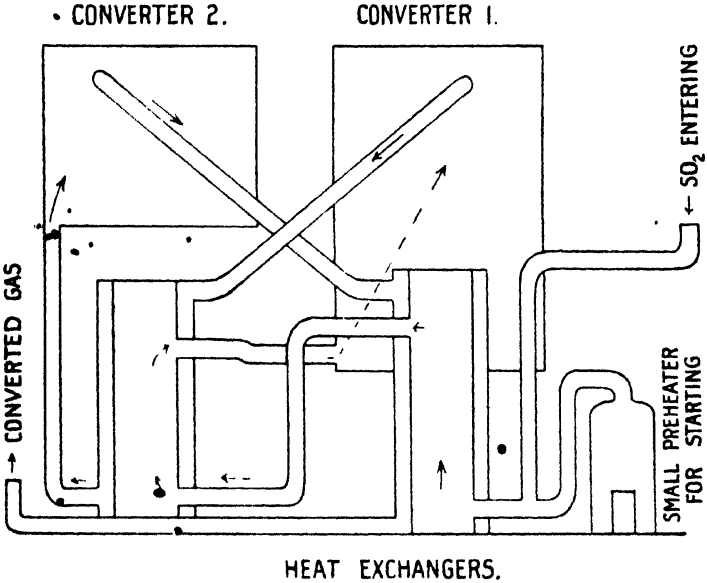


FIG. 33.—Arrangement of duplicate Converters and Heat Exchangers.

in two stages, only half the platinum formerly used is required, and in each converter is only one-quarter of that which was placed before in a single converter. The conversion in the first converter should be from 80 to 90 per cent. In some cases as much as 70 per cent. of the platinum can be dispensed with. If under ordinary conditions with a single converter 100 parts convert to the extent of 97 per cent., about 80 per cent. of this is done by 15 parts of the metal, the remaining 17 per cent. requiring all the catalytic activity of the other 85 parts.

The arrangement of the two converters and their heat exchangers is shown in Fig. 33, which is a diagram of the

conversion system of the four 20-ton units of the Bäyer plant at Dormagen. The conversion in the first vessel has been observed to be from 76 to 78 per cent., and that in the second from 96 to 97 per cent., the overall conversion being therefore 99 per cent. Each converter contained a number of sections packed with asbestos fibre. So far as is known this carrier is used on all plants of this type, although there appears to be no reason to believe that Grillo mass could not be substituted for it. A similar arrangement was reported to be in operation at the Höchst works of Meister, Lucius and Brüning, in 1919. The first converter was said to work at 580°, the second at 435°, and with an inlet gas of 6·5 per cent. a total conversion of 97·7 per cent. was obtained. It will be noted that the inlet gas passes first through the heat exchanger attached to the second (and cooler) converter. The use of two heat exchangers in succession in this way makes the heat regeneration easier to carry out than with a single one, and during operation no external heat need be applied.

In Fig. 34, which shows the connection of the conversion and absorption systems of an American *Badische* plant, the same features will be noticed.[1]

The Höchst works found that the advantages of the multiple conversion were greatly increased by removing the sulphur trioxide formed after the first conversion. This procedure was patented in 1901 (B. P. 2368 of 1901) and can readily be seen (from other than practical considerations) to be a sound one, for not only does the removal of trioxide tend to give a higher conversion at equilibrium by increasing the ratio of the oxygen to the sulphur compounds, but, as has been shown by Bodenstein and others, the velocity of reaction also will be greater if the trioxide is removed. Before absorption of the trioxide could be carried out the gases would require cooling, and it seems questionable whether in any circumstances the gain in conversion, or saving in platinum, would outweigh the loss of heat due to the additional cooling process. The arrangement of a section of plant is shown in Fig. 35. Gas first enters the first contact space O_1 after suitable preheating. After the greater part of the sulphur dioxide has been transformed it passes into the heat exchanger V_1, and

[1] *U.S. Bureau of Mines*, 1920, *Bull.* 184.

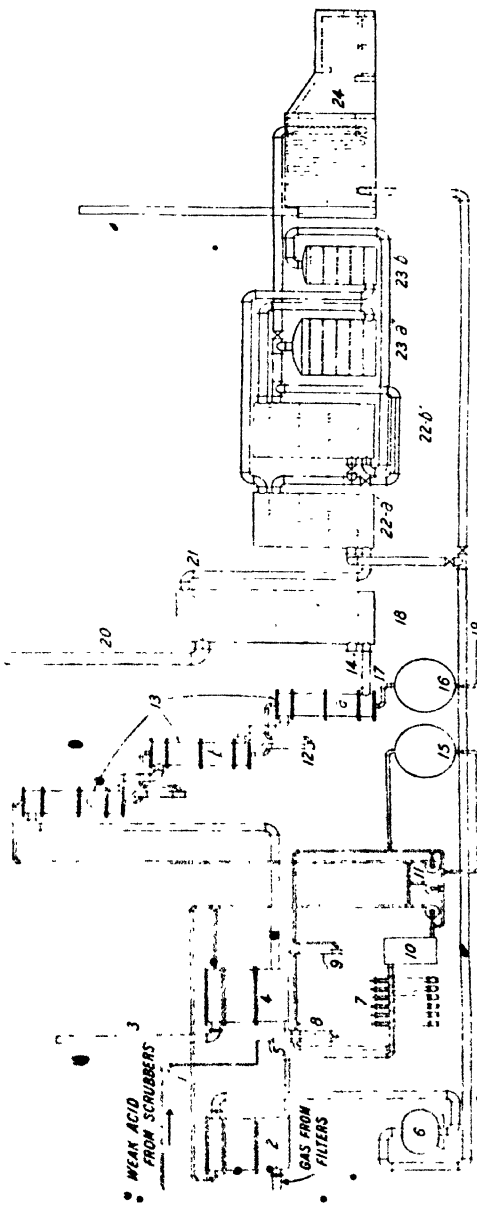


FIG. 34.—Badische System, Flow Chart.

1, sight feed; 2, drier; 3, waste gas stack; 4, absorber; 5, weak acid inlet; 6, blower; 7, cooler; 8, strong acid overflow; 9, cooler; 10, tank; 11, pump; 12, acid cooler; 13, *a*, *b*, *c*, oleum towers; 14, air inlet; 15, tank for 99 per cent. acid; 16, tank for oleum; 17, SO_3 gas (cold); 18, SO_3 gas cooler; 19, to loading station; 20, stock; 21, SO_3 gas (hot); 22, *a*, *b*, heat exchanger; 23, *a*, *b*, converter; 24, preheating furnace used in starting.

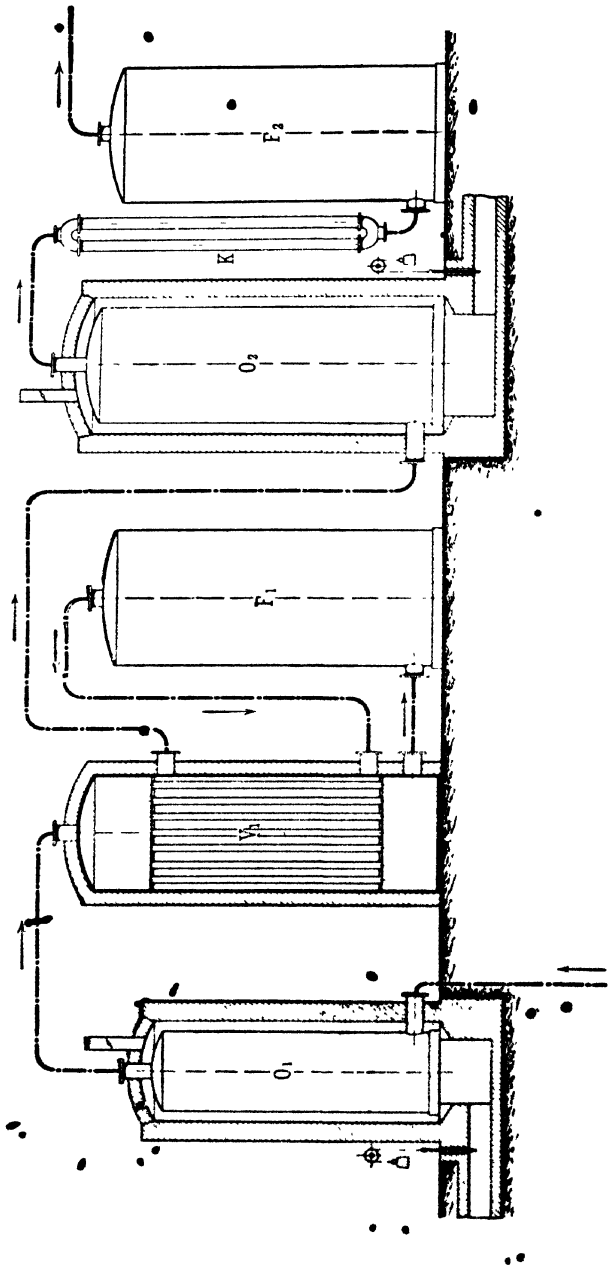


FIG. 35.

after cooling in this, into the absorber F_1. From this it is carried back to the heat exchanger then to the second converter O_2, finally via a cooler K to the second absorber F_2. It is doubtful whether this system is now anywhere in use.

The admission of cold gas to the contact space, first patented by the Höchst works,[1] has been frequently used on all types of plant. All that is generally necessary is to arrange for bye-passing the preheating and heat-exchanging sections of the plant to the necessary extent, so that the temperature of the inlet gas can be nicely controlled. As a means of controlling sections of a converter it is not of much use, for the effect of any cooling is diminished by the increase of load on the section treated. In patents of 1903 (B. P. 6824 of 1903; U.S. Ps. 723595, 723596) the gradual dilution of concentrated gas by air in multiple converters is claimed. It is preferable to work with gas containing about 11 per cent. of dioxide, which is partially converted in the first chamber, then mixed with more air and passed to the second, and so on.

Other patents in connection with the control of conversion: Raynaud and Pierron, B. P. 16254 of 1900, separate converters at different temperatures; Babatz, B. P. 1216 of 1901, heating of pure gases by hot flue gases; Daub and Deuther, B. P. 9536 of 1902, alternate layers of mass and cooling elements; Sébillot, B. P. 21616 of 1898, sulphuric acid from blast-furnace gases; Sébillot, B. P. 2192 of 1909, catalysis of dilute gases from roasters; Wischin, B. P. 12419 of 1903, arrangement of contact-mass.

Preheating and Heat-Regeneration.

There are three sources from which may be supplied the heat necessary for raising the temperature of the gas entering the converter to the requisite point. (1) The gas may be passed through a preheater in which coal or other fuel is burnt. This is the oldest method and is always necessary when a plant has to be started if the contact-mass is cold. It is also in use in some cases for regular running, although in modern practice there is no need for the consumption of any fuel at all. (2) The heat of reaction may be transferred from the gas leaving the converter to that entering it. As will be more clearly seen

[1] *Loc. cit.*, p. 153.

when the subject is referred to later, this heat is always sufficient, with appropriate design, for the purpose in view. (3) The heat of combustion of the pyrites or sulphur may be transferred in the same way. Methods (2) and (3) are sometimes combined. The usual type of Mannheim plant uses both, and (1) in addition.

The elements of plant by which all these heat transferences are carried out receive different names in different works. It will be convenient to distinguish in a general way (1) *Preheaters* in which fuel is burnt, and (2) *Heat Exchangers* in which hot gas passing through the plant is the heating agent. "Superheater" is a common name for a preheater which is placed after heat-exchange apparatus. Other names show perhaps less reason than variety.

Preheaters. — A type of preheater which is in extensive use is that illustrated in Fig. 36. The tubes are of cast-iron and are cast in U-shape, the length being from 7 to 8 ft. and the inside diameter from 4 to 6 in. The wall thickness is from $\frac{3}{4}$ to 1 in. The gas is delivered from a header into a number of these tubes in parallel, and these are connected in series with other tubes by means of return bends. Flanged connections are not used because the exposure to the heat would not allow of the joint remaining tight, and the connection is made by casting a shoulder about an inch wide round the ends of the tubes and building up a rust joint in a sleeve placed on this shoulder. This shoulder is shown in Fig. 37. The cast-iron ring is about $1\frac{1}{2}$ in. larger in bore than the outside of the pre-heater tubes, about $\frac{3}{4}$ in. thick, and about 5 in. high. The rust joint made by tamping in a mixture of sal-ammoniac and iron is strong and does not leak when heated. In refitting the tubes the cast-iron rings are broken with a hammer as the jointing cannot readily be extracted. It will be noticed that each tube has a pedestal cast on to it, and is supported from above by means of a tie-rod fastened to a boss at the top of the bend.[1]

In Fig. 90 (which actually represents a heat-exchange installation) is shown a somewhat similar construction, but for several reasons the arrangement is superior to the last. The tubes are suspended in this also by tie-rods which are

[1] *U.S. Dept. of Int. Bull.* 1920, **184**, 167.

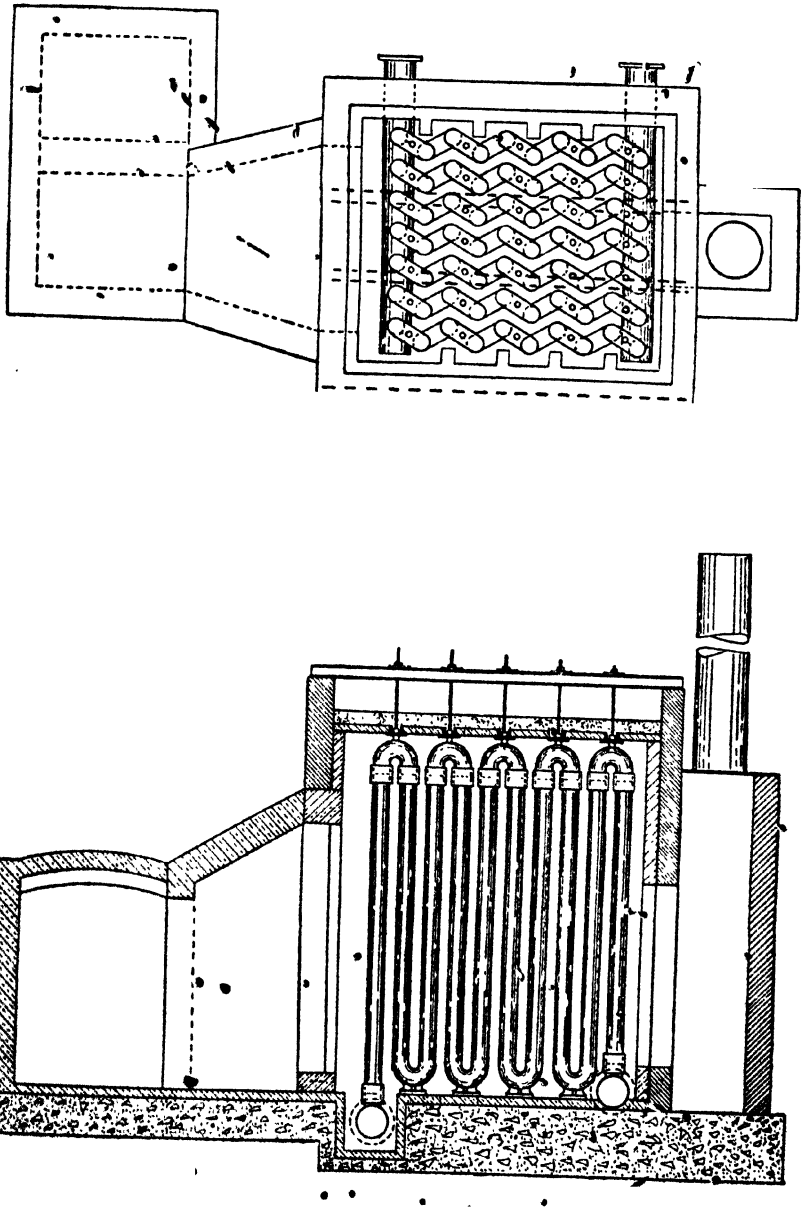


FIG. 36.—U-pipe Preheater.

attached not to the bends, but to a feather cast between the two pipes below the flanges. The joints are entirely removed from the hot zone and are packed with non-conducting material in the usual way. The whole weight of the pipes, and of the tiles and insulation, is borne by the tie-rods. The lower ends are quite free. This design was used in the preheaters of the Grillo plants at Gretna and Queen's Ferry, and has been adopted elsewhere. Each preheater (two to each unit) contained two chambers, in each of which were twenty-four U-pipes 8 ft. 6 in. long, of 5 in. internal diameter and $\frac{3}{4}$ in. thick.

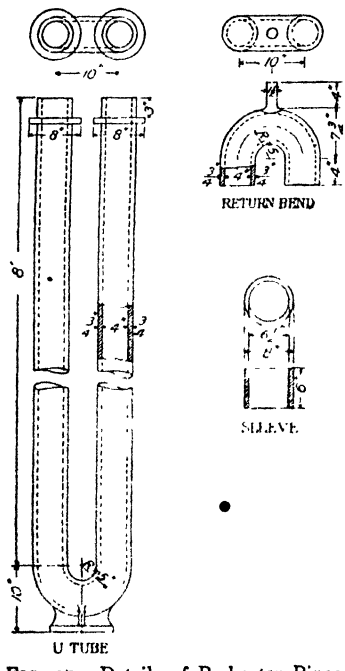


FIG. 37.—Details of Preheater Pipes.

It will be noticed from any of the figures that the vertical plane of any pipe is inclined to the general direction of flow. This placing of the return bends results in each cross-row of pipes being staggered in relation to those behind and before it, and in a greater heating effect. In addition it is usual to pass the cold gas through the pipe in counter-current to the hot gas. The furnace products are not allowed to pass directly on to the tubes. For the preheater similar to Fig. 90 there are two furnaces, and the gas from these passes into a combustion chamber which is common to both preheater chambers and connected with them by vertical slits in the partition wall. This type of preheater operates with very little trouble, and with joints outside the chamber, leaks are readily detected and repaired. It is not possible to give any general figures for the fuel consumption, as the duty of the preheater varies greatly, and is in most cases only occasional. The thermal efficiency, however, is low whenever coal or coke is employed. Oil firing is said to be more efficient. The preheater of Fig. 36 is shown with a firebox for burning crude oil.

Another type of preheater is that used on the Tentelew plant. It consists of a number of steel tubes about 3½ in. bore set in a square cast-steel header. Into a tube plate which divides the header horizontally are set an equal number of narrower tubes, each of which passes almost to the bottom of a larger one, in the manner of Field boiler tubes. For a production of 10 or 12 tons of trioxide, over 100 of these tubes are used, each about 8 ft. long. The preheater is set in a brick furnace, forming a very compact structure, and is usually fired with coal (see Fig. 113, p. 367).

The figures below give some indication of the magnitude of the provision for preheating on three types of plant. They relate in each case to the external heated area of the preheater:—

Plant.	Approx. Production in tons SO_3 / day.	Exposed Preheating Area.
Grillo .	22·5	2880
Tentelew .	11·0	1000
Mannheim .	5·0	80

Heat Exchangers.—When the heat in the gas passing from the converter is to be recovered by the entering gas, tubular

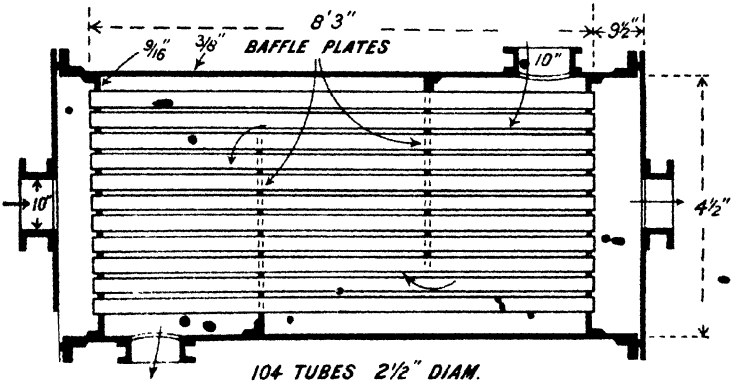


FIG. 38.—D. E. S. Heat Exchanger.

heat exchangers are always used. The construction of these may be seen from Fig. 38, which represents an exchanger inserted after the platinum contact of a Grillo or Mannheim plant. There are two internal tube plates, and into these

are expanded 100 steel tubes of 2½-in. bore. Two baffle-plates, through which the tubes are passed, cause the gas passing over the tubes to take a zigzag course between the two orifices. The converted gas containing trioxide usually passes through the tubes, although there are exceptions to this. The tubes can be cleaned in the inside by removing the end covers and driving cleaning bars through them, whereas the outsides are impossible to reach. The efficiency of heat transference is to a large extent dependent on the state of the tube surfaces. The lagging of the whole vessel should be thorough in order to reduce the heat loss as far as possible.

Additional examples of similar construction will be found illustrated in Fig. 39, and in the Tentelew "regulator" attached to the converter in Fig. 25. The first of these contains not only baffle-plates, but in addition has gas chambers by which the direction of the gas in the pipes may be changed as well as that of the gas outside. The path of the gas is shown by arrows. There are three changes of direction, so that the path of the converted gas is four times as long as in the first example of Fig. 38. Such an exchanger would have about 200 tubes of 2-in. bore. It is completely lagged by insulating material packed into a surrounding vessel of sheet-iron.

The second example, the illustration of which is copied from the Tentelew patent and shows the connection with the converter, is of interesting construction. The number of tubes is often over 300, and the allowance of cooling surface for unit weight of gas is high. The converter exit-gas passes upwards through the central pipe and downwards through the surrounding tubes, the incoming gas ascending outside in counter-current. With this element of plant the recovery of heat can be made so complete that, other conditions being favourable, regenerative running (*i.e.*, running without heat from fuel or from combustion of the pyrites) is regularly possible. The heat recovered may, in fact, be too much, and by means of the valve at the bottom, a fraction of the hot gases may be by-passed to the main without going through the heat exchanger. The conditions for completely regenerative running are referred to below.

Fig. 90, which has already been referred to, represents the "heater cooler" of a D.E.S. Grillo plant. "There were in all

six rows of eight U-pipes, heated by the sulphur burner-gases, which left the burners at from 550° to 650°, and by passing outside the tubes and through some connecting flues of brick,

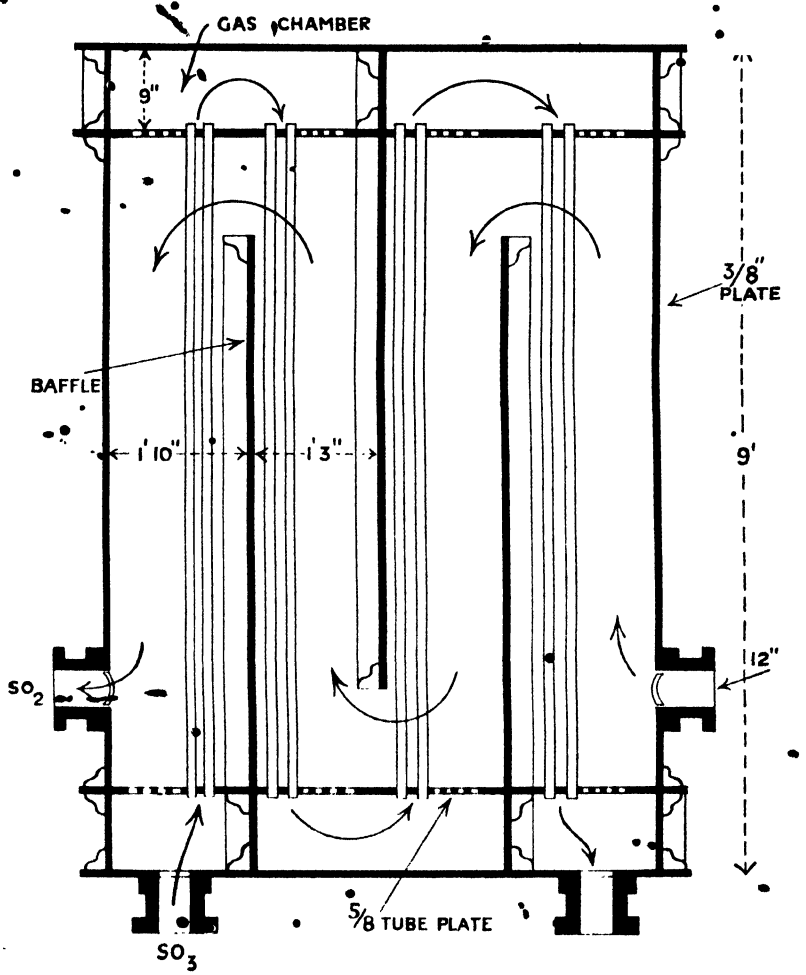


FIG. 39.—Baffled Heat Exchanger.

were cooled to about 300° at the entrance to the leaden gas-cooler. The construction and dimensions were exactly similar to those of the preheater which has already been described. In operating this kind of heat exchanger it is always necessary, for reasons of safety alone, to maintain such a

temperature that no acid can condense either on the outside or the inside of the pipes.

Theoretically, if a heat exchanger were very long and were operated on the counter-current system, all the heat which the first gas-stream had in excess of the second should be transferred to the second stream in one passage through the exchanger. In practice with exchangers of the dimensions shown in Fig. 38, the cold gas becomes heated to a temperature which is about the mean of the two initial temperatures. To gain much more than this it would be necessary either to lengthen the apparatus considerably, or to have two exchangers in series.

In the table given on page 181 some representative figures relating to various types of heat-exchange apparatus, all of which are illustrated, have been set out. It should be borne in mind that on each plant all the types mentioned may be used at once, and that in the case of the Mannheim plant it is usual to heat the gas over the final range of 100° or 50, by an additional coal or coke-fired preheater.

Regenerative Operation.—If the converter with its internal or external heat exchangers be regarded as a single system, it becomes clear that, neglecting heat losses, the necessary temperature in the converter can be maintained only if the heat carried away in the outgoing gas (diminished by the heat carried in by the incoming gas) is less than or equal to the heat of reaction. If the specific heats of the gas mixture before and after conversion are taken as the same (an almost necessary assumption which is not far from correct), the rise of temperature due to a 95 per cent. conversion is found to be, for a gas containing 5 per cent. of sulphur dioxide, 141°; for a 7 per cent. gas, 193°; and for a 10 per cent. gas, 281°. It follows, therefore, that the system will gain heat if the converted gas leaves it at a temperature which exceeds that of the incoming gas by less than 141°, 193°, or 281°, in the three cases. This makes it clear that the necessary recuperation will be more readily performed the higher the percentage of sulphur dioxide. Dissipation of heat from the converters and exchangers modifies these figures considerably, without altering the principle. Heat exchange is naturally less difficult the higher the final permissible temperature of the converted gas,

Heat-Exchange Apparatus—Data.

	Description of Heat Exchangers.	External Surface of Heating Pipes, in square feet	Weight of Gas Mixture heated, in lb. per hour.	C.H.U. transferred to cooler gas per hour through 1 sq. foot of External Exposed Surface.	Temperature of cooler gas.		Temperature of hotter gas.	
					Entry.	Rise.	Entry.	Fall.
I.	Mannheim Plant. 2 Heat Exchangers. 100 steel tubes in each. 8 ft. 3 in. long × 2¾ external diameter. ⅛ in. thick, on 2 tube plates 4 ft. 2 in. diameter	1240 (total)	3750 (3750 cooled)	160	15	225	480	250
II.	Grillo Plant. 2 similar Exchangers	"	12260 (15530 cooled)	353	35	154	429	144
III.	Mannheim Plant. 2 "Forewarmers." Heated by gas from oxide shafts, each having 12 C.I. pipes 10 in. internal diameter and bends	160 (total)	3750 (4020 cooled)	712	240	130	510	145
IV.	Grillo Plant. "Heater-Cooler." Heated by sulphur burner-gas. 48 C.I. pipes (U) 5 in. internal diameter, ¾ in. thick	1240	(i) 15730 (9520 cooled)	347	191	136	590	314
			(ii) 12260 (7995 cooled)	375	189	219	753	412
V.	Tentelew Plant. "Regulator." Heated by exit gases from converter. 320 steel tubes 12 ft. 8 in. long × 2 in. external diameter, ¼ in. thick	2200	5350	106	25	190	410	...

so that for regenerative running a gas concentration of 6·5 to 7·5 per cent. (occasionally even higher) is a great advantage and is frequently maintained. Such a concentration, of course, implies an arrangement of the contact-mass by which the temperatures in the converter are prevented from rising too far, and is probably more readily dealt with (and more economical distribution of platinum secured at the same time) by means of the system of duplicate converters which has already been mentioned.

The requirements for regenerative operation are therefore: (1) very efficient heat-insulation; (2) efficient heat exchange; and (3) fairly high sulphur dioxide concentration. If, in addition to the heat of the gas reaction, the heat set free by the combustion of the raw material can be drawn on, the problem becomes much more simple, for the high temperature of the gas from pyrites-burners, even when it contains only 5 per cent. or so of sulphur dioxide, is well known to everyone. Even with sulphur, when the heat of combustion (per unit of sulphur) is only about three-quarters as much as in the former case, sufficient heat is set free to raise, on the basis of Berthelot's figure, a 7 per cent. gas mixture to 630° and a 10 per cent. mixture to 860°. Actual temperatures of sulphur burner flues are often between 600° and 700°. From such sources of heat the gas can be heated nearly or entirely to the temperature at which conversion begins, and the regeneration of heat from the converted gas becomes a matter of far less importance.

Of all types of plant which are known to be operated in this country, with the possible exception of one or two about which information is unobtainable, the Tentelew is the only one which works without either consumption of fuel or utilisation of the sensible heat of the burner-gas.

The Estimation of Percentage Conversion.

The estimation of the degree of conversion usually forms part of the normal routine of a contact plant, sufficient tests being made from time to time to make certain that each converter is doing the work expected of it. The actual control is to a large extent dependent, in most cases, on the temperatures indicated by thermometers placed in, or near the catalytic

mass, but conversion tests are nevertheless required with a frequency which varies from plant to plant and with the conditions of operation.

Three lines may be followed in making these tests. *Method* 1—The percentage of sulphur dioxide may be determined before and after conversion. This is the most usual and the most accurate way. *Method* 2—The percentages of sulphur dioxide and of the oxygen remaining may be determined after conversion. The calculation here depends on some not very certain assumptions regarding the amount of oxygen consumed in the combustion of the pyrites or sulphur, but the procedure is very useful where the first cannot be adopted. *Method* 3—The ratio of sulphur trioxide to dioxide is found for the converted gases. This seems simple, but in practice there are great difficulties. It is almost impossible to absorb sulphur trioxide in an aqueous solution rapidly and completely without cumbrous apparatus, and it is never quite certain that all the trioxide has passed uncondensed through the inlet tubes of the apparatus. The dissolved dioxide also is oxidised by the oxygen present, and the results are vitiated. This method is occasionally used, but will not be referred to further.

To make simultaneous determinations of sulphur dioxide in the gases entering and leaving the converter is a more straightforward matter, and although certain precautions are necessary, the results may be obtained with considerable accuracy. For this purpose the Reich method has been most commonly used and received considerable attention and amplification. It will therefore be discussed in detail, particularly with regard to the special precautions which are made necessary by the presence of sulphur trioxide. The Reich test in its usual form lasts only about five minutes, and to meet the need for a test averaging the conversion over a period of hours, "continuous" tests are often made which will be referred to later.

It is sometimes the practice to obtain one of the samples from the gas leaving the absorbers, *i.e.*, from the gas after removal of the trioxide formed. By this choice of sampling places it is made possible to obtain, in each case, gas free from trioxide. Testing becomes a simpler matter, and aspiration tests can be made without trouble; but the procedure is not

otherwise a good one, for absorption of dioxide by the acid in the absorbers, and other causes, are liable to alter the proportion of dioxide from the value it had at the converter outlet. As the object of the test is to evaluate the performance of the converter, the sampling places should in every possible case be at the converter inlet and exit. The sampling pipes should all be at the same height (4 ft. 6 in. from the ground is convenient), and should all project (without bends) from the main pipes in the direction of the right hand of the tester, *i.e.*, he should always have the main pipe on his left. A piece of ¾-in. pipe, long enough to project about 1½ in. beyond the surface of the lagging, is tapped into the main pipe, and into the ¾-in. pipe is fixed a 6-in. length of ⅜ or ½-in. pipe, the outer end of which has been tapered down to take the rubber connection.

These sampling pipes may be fitted with a cast-iron plug-cock; but as this involves more trouble in cleaning, it seems at least equally satisfactory, if the pressure inside the converter is not too high, to close the tapered end of the pipe with a piece of rubber tubing and glass rod, when tests are not being made. When new fittings are put in they must be freed from all traces of grease. This can be done most readily by heating each part to redness in a fire, and then making the connections with silicate of soda. If this is not done, an exit sampling pipe may cause the trioxide to be reduced and the unconverted dioxide to appear absurdly high, for several weeks.

The Reich Test (*Method* 1).—Suitable apparatus is shown in the sketch. *C* is the iron sampling pipe. Through the rubber tube *r*, closed when not in use by a short length of glass rod, passes a narrow glass tube *t*. The use of this glass tube avoids contamination by the dirt which always lodges in the iron pipe. On a high-pressure system such as the Tentelew, this glass tube and the rubber stoppers could not be applied and removed without great difficulty, and the iron sampling-pipe with a stop-cock must be relied on. It should be cleaned and replaced before each series of tests. A wide-mouthed clear glass bottle of 200 c.c. capacity (*b*) is suitable as an absorption vessel. An inlet and an exit tube should be fixed in by means of a double-holed rubber stopper. The inlet tube descends to within ¼ in. of the bottom of the bottle and is drawn out at the

end to a fine point. About an inch above the rubber stopper it is bent at right angles, and the horizontal portion, which should be about 4 in. long, carries a glass stop-cock. The aspirator (*a*) should hold about 2 litres and may be replaced, with slight modification, by a Winchester quart bottle. It is fitted with a

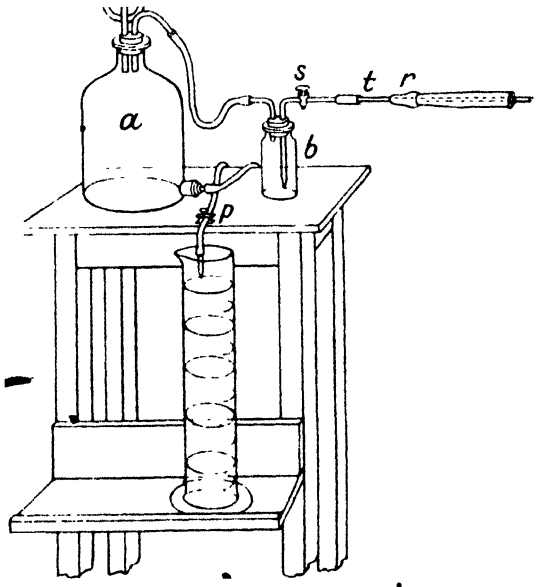


FIG. 40.—Apparatus for Conversion Tests.

siphon, each limb of which is longer than the height of the water in the aspirator at starting. The run-out tube for the water carries a pinch clip (*p*) and ends in with a short length of glass tube drawn out to a point. Decinormal iodine solution is required for the inlet test. Centinormal iodine solution should be made from this daily, using an accurate 25 c.c. pipette and an accurate 250 c.c. flask. Great care should be

taken that both these solutions are kept in the coolest available place. Centinormal iodine which is allowed to become warm loses strength very rapidly.

The stronger solution should be accurately decinormal, but a slight inaccuracy here does not affect the figure obtained for the conversion, if the above instructions are followed, for the very reason that it affects the estimation of dioxide at inlet and exit, and renders them inaccurate in the same ratio.

Starch solution should be perfectly clear (paste is of very little use) and should be made afresh each day.

To make a test, the glass inlet tube and stop-cock are first made thoroughly clean and dry. (It is convenient to dry them by allowing hot gas from the inlet side of the converter to stream through.) The aspirator is filled up, the cork inserted and water run to waste by opening *p* until the water in the siphon stands level. Fifty c.c. of water and 5 c.c. of the starch solution are put into the absorption bottle, and the iodine solution added. The glass inlet tube is connected to the tube *t* by means of a 2-in. length of new black rubber tube, so that both tubes are in actual contact, the glass stop-cock being closed. The clip on the outlet tube of the aspirator is then opened and water run out into the cylinder. If the flow of water does not stop altogether in a short time, the apparatus leaks and must be repaired. The flow having stopped, begin the test, opening the stop-cocks far enough to cause the bubbles to pass so quickly that they can hardly be counted, but not so fast as to appear a continuous rush of gas. Give the absorption bottle a swirling motion all the time the gas is passing. When the solution turns deep blue, bubble more slowly, and as the colour lightens pass only a bubble at a time until the liquid is a faint lavender blue. This is the best end-point. Let the run-off tube from the aspirator dip into the water in the cylinder, and then raise the cylinder to allow water to run back into the aspirator until the manometer stands level again. Put the pinch-cock on the water-tube and note the number of cubic centimetres of water in the cylinder. Pour this water back into the aspirator.

For the first preliminary test use only about 2 or 3 c.c. of iodine solution. After this add *exactly* 10 c.c. and go on again, repeating until the results are consistent.

It must always be borne in mind that, although these tests are simple in principle, they require both care and practice. Too much attention cannot be paid to the cleanliness of any article which is in contact with the free trioxide. If the manipulation is not of the best, the inlet tests tend to give high results and the exit tests low ones, so that conversion is apparently too high. When the sulphur dioxide percentage at the inlet exceeds 6, or when it exceeds 0·6 at the exit, it is advisable to use 20 c.c. of iodine solution instead of 10, thus increasing the volume of the water run out, otherwise too small for accurate reading. Each test should last four to five minutes. A series of experiments made by the writer showed that under these conditions the amount of dioxide passing unabsorbed was inappreciable. To use excess of iodine and titrate back is therefore unnecessary. It was also found that the mere presence of trioxide in the gas under test was quite without results, identical figures being obtained in parallel experiments run with and without its removal.

In place of the expensive potassium iodide which is in general use for the solution of the iodine, caustic soda may be used, as has been shown by Lowe[1] in experiments carried out on a contact plant. The modified solution contains 635 gm. iodine, 150 to 180 gm. caustic soda, and water up to 50 litres. From this N/10 solution the whole of the iodine is liberated by adding acid, and the addition of the sulphur dioxide alone in the inlet test provides all the acidity required. In the exit test the addition of a little sulphuric or hydrochloric acid is found to be necessary.

Calculation of Results.—As will be shown on page 190, the percentage conversion is most conveniently obtained from the results of the Reich tests immediately, without reference to the dioxide percentages. But dioxide estimations are frequently required, and for this purpose the tables below may be used. They are calculated on the basis that 10 c.c. N/10 iodine solution absorb 10·93 c.c. SO_2 at 0° and 760 mm.

The percentages being known from the two Reich tests, the conversion can now be calculated. The percentage actually found at the converter inlet will be noted by *a*, that at the exit by *b*. If the 100 vols. in which *b* vols. of sulphur dioxide

[1] *J. Soc. Chem. Ind.* (*Trans.*), 1921, 40 [illegible]

were found had actually contained a vols. before conversion, the percentage conversion would be given by the equation—

$$c = \frac{100\,(a-b)}{a} \quad . \quad . \quad . \quad (1),$$

but this is not the case, for the total volume of the gas has diminished between the two tests. Suppose that a vols. of

Inlet Test, 10·00 c.c. N/10 *Iodine.*

c.c.	Per cent. SO_2 at				c.c.	Per cent. SO_2 at			
	10°.	15°.	20°.	25°.		10°.	15°.	20°.	25°.
100	10·20	10·34	10·50	10·66	260	4·16	4·25	4·32	4·39
110	9·34	9·48	9·64	9·79	265	4·10	4·17	4·24	4·31
120	8·63	8·77	8·91	9·04	270	4·03	4·09	4·16	4·23
130	8·02	8·15	8·28	8·41	275	3·96	4·02	4·09	4·16
140	7·40	7·61	7·73	7·85	280	3·89	3·95	4·02	4·09
150	7·02	7·14	7·25	7·37	290	3·76	3·82	3·89	3·95
155	6·81	6·92	7·04	7·15	300	3·64	3·70	3·76	3·82
160	6·61	6·72	6·83	6·94	310	3·53	3·59	3·65	3·71
165	6·43	6·53	6·64	6·74	320	3·42	3·48	3·54	3·59
170	6·25	6·35	6·45	6·56	330	3·33	3·38	3·43	3·49
175	6·08	6·18	6·28	6·38	340	3·23	3·28	3·33	3·39
180	5·92	6·02	6·12	6·22	350	3·14	3·19	3·24	3·30
185	5·77	5·87	5·96	6·06	360	3·05	3·10	3·16	3·21
190	5·63	5·72	5·81	5·91	370	2·97	3·02	3·07	3·12
195	5·49	5·58	5·67	5·77	380	2·89	2·94	2·99	3·04
200	5·36	5·45	5·54	5·63	390	2·82	2·87	2·92	2·97
205	5·24	5·33	5·41	5·50	400	2·75	2·80	2·85	2·90
210	5·12	5·20	5·29	5·38	410	2·69	2·74	2·78	2·83
215	5·01	5·09	5·17	5·26	420	2·63	2·67	2·72	2·76
220	4·90	4·98	5·06	5·14	430	2·57	2·61	2·66	2·70
225	4·79	4·87	4·95	5·04	440	2·51	2·55	2·50	2·64
230	4·69	4·77	4·85	4·93	450	2·46	2·50	2·54	2·58
235	4·60	4·68	4·75	4·83	470	2·35	2·39	2·43	2·48
240	4·51	4·58	4·66	4·74	490	2·26	2·30	2·34	2·38
245	4·42	4·49	4·57	4·64	510	2·17	2·21	2·25	2·29
250	4·34	4·41	4·48	4·55	540	2·05	2·09	2·13	2·16
255	4·25	4·33	4·40	4·47	570	1·95	1·98	2·02	2·05

dioxide were originally present in 100, and that the conversion has been c per cent. Then $ca/100$ vols. of trioxide were formed and $(100-c)a/100$ vols. of dioxide remain. But from the original 100, the combination of oxygen has caused $ca/200$ vols. to disappear, and since the trioxide also practically disappears during the test the 100 vols. have

shrunk to $100-3ca/200$. The actual percentage of dioxide now is—

$$b = \frac{(100-c)a}{100-3ca/200}.$$

and from this we obtain-

$$c = \frac{100(a-b)}{a(1-0.015b)} \quad . \quad . \quad . \quad (2).$$

Exit Test, 10·00 c.c. N/100 *Iodine*.

c.c.	Per cent. SO_2 at				c.c.	Per cent. SO_2 at			
	10°.	15°.	20°.	25°.		10°.			25°.
170	0·662	0·674	0·685	0·697	330	0·342	0·348	0·354	0·360
175	0·643	0·655	0·666	0·677	340	0·332	0·338	0·344	0·350
180	0·626	0·637	0·648	0·658	350	0·323	0·328	0·334	0·340
185	0·609	0·621	0·630	0·641	360	0·314	0·319	0·325	0·330
190	0·593	0·603	0·614	0·624	370	0·305	0·311	0·316	0·321
195	0·578	0·588	0·598	0·608	380	0·297	0·303	0·308	0·313
200	0·563	0·573	0·583	0·593	390	0·290	0·295	0·300	0·305
205	0·550	0·559	0·569	0·579	400	0·282	0·287	0·292	0·297
210	0·537	0·546	0·556	0·565	410	0·276	0·280	0·285	0·290
215	0·524	0·533	0·543	0·552	420	0·269	0·274	0·278	0·283
220	0·512	0·521	0·530	0·539	430	0·263	0·267	0·272	0·277
225	0·501	0·510	0·519	0·527	440	0·257	0·261	0·266	0·270
230	0·490	0·499	0·507	0·516	450	0·251	0·256	0·260	0·264
235	0·480	0·488	0·497	0·505	470	0·240	0·245	0·249	0·253
240	0·470	0·478	0·486	0·495	490	0·231	0·235	0·239	0·243
245	0·460	0·468	0·477	0·485	510	0·223	0·226	0·229	0·233
250	0·451	0·459	0·467	0·475	540	0·209	0·213	0·217	0·220
255	0·442	0·450	0·458	0·466	570	0·198	0·202	0·205	0·209
260	0·434	0·442	0·449	0·457	600	0·189	0·192	0·195	0·198
265	0·426	0·433	0·441	0·448	630	0·180	0·183	0·186	0·189
270	0·418	0·426	0·433	0·440	660	0·171	0·174	0·177	0·180
275	0·410	0·418	0·425	0·432	700	0·162	0·164	0·167	0·170
280	0·403	0·410	0·417	0·424	750	0·151	0·154	0·156	0·159
285	0·396	0·403	0·410	0·417	800	0·141	0·144	0·146	0·149
290	0·389	0·396	0·403	0·410	850	0·133	0·135	0·138	0·140
300	0·376	0·383	0·390	0·396	900	0·126	0·128	0·130	0·132
310	0·364	0·371	0·377	0·383	950	0·119	0·121	0·123	0·125
320	0·353	0·359	0·365	0·371	1000	0·113		0·117	0·119

When only approximate results are required, the first equation, is sometimes sufficient, but for accuracy the second must always be employed. The error involved in using (1) is of course the greater the higher the value of b. It is, for instance, in the case when $a=5·5$, 0·16 at 98 per cent. conversion,

0·32 at 96, 0·47 at 95, 0·75 at 90, 1·07 at 85, 1·33 at 80, and correspondingly more for lower conversions.

The calculation of c from equation (2) is a troublesome affair when conversion tests are a matter of daily routine. Tables for the purpose have been constructed, but are necessarily extensive and cumbrous if they are to be of practical use, and are, in addition, difficult to interpolate from quickly unless more extensive than have yet been made. The construction of charts is the best solution of the problem, and examples of two are given. Fig. 41 is intended for ascertaining c directly from the results of the Reich test, but can also be used to ascertain it from a and b, if these are known. It is only necessary to stretch a fine thread across the diagram between the points representing a and b on the vertical scales. The intersection of the thread with the middle scale then defines c. Fig. 42 is given in illustration of a chart specially made to give c from known values of a and b.[1] It should be constructed for use on a much larger scale, and if only a certain range of a or b, or both, is required, can easily be restricted to this range. The precision of these charts, for instance that shown in Fig. 41, can be made sufficient for all practical purposes, and for conversions above 90 is about 0·1 per cent.

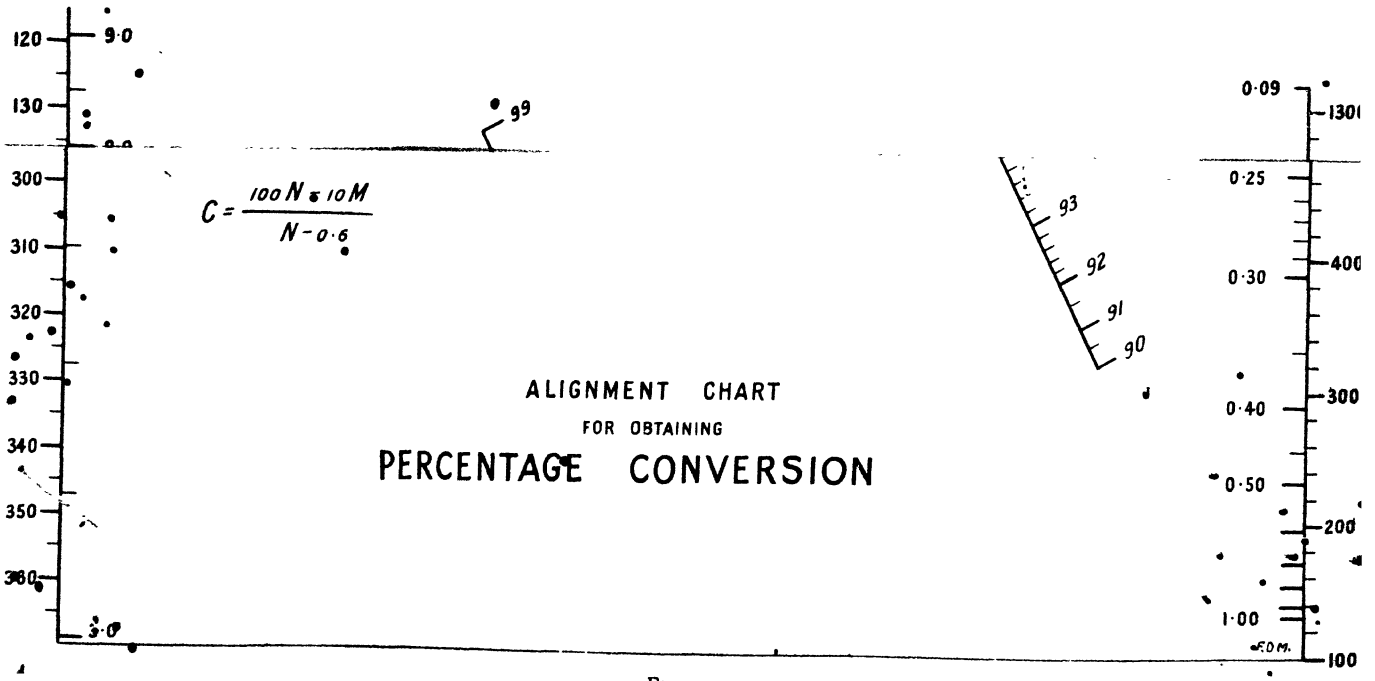
Suppose that in the Reich tests M and N c.c. of water have been run out at inlet and exit respectively. At 20°, which we may take to be the average temperature of the tests, 10 c.c. of N/10 iodine absorb 11·73 c.c. of SO_2, the pressure being 760 mm. We have, therefore—

$$a = \frac{11.7 \times 100}{M + 11.7} \text{ and } b = \frac{1.17 \times 100}{N + 1.17},$$

and if these values of a and b are inserted in the conversion equation (2) and the result worked out, it appears that—

$$c = \frac{100N - 10M}{N - 0.6} \quad \ldots (3).$$

[1] *Note on Construction of Fig.* 42.—To construct a chart of this kind first of all set out c_1 (*i.e.*, $100(a - b)/a$), and b on the parallel axes, to uniform scales. The axes may be any convenient distance apart. The support for a passes through the points $(b, 0)$ and $(c_1, 100)$, and the graduations on it are obtained by projecting those of c_1 on to it with suitable points on the b axis (*e.g.* b, 5) as radiant points. The support for c passes through the point $(c_1, 0)$ and would pass through the point $(b, 66.6)$ if produced, and is laid out accordingly. To graduate it, the graduations of c_1 are projected on to it with $(b, 0)$ as radiant.



ALIGNMENT CHART

FOR OBTAINING

PERCENTAGE CONVERSION

FIG. 41.

[Face page 190.

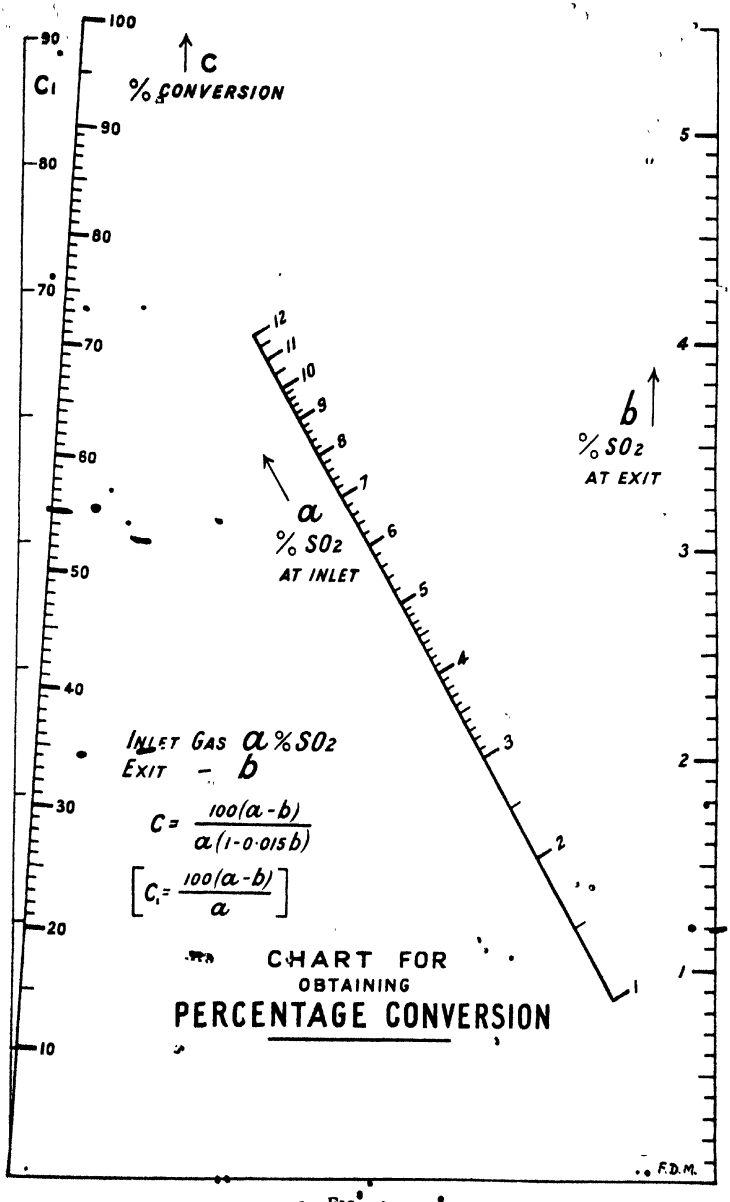

C
% CONVERSION
C1
100
90
80
70
60
50
40
30
20
10
a
% SO2
AT INLET
12
11
10
9
8
7
6
5
4
3
2
1
b
% SO2
AT EXIT
5
4
3
2
1
INLET GAS a % SO2
EXIT - b
C = 100(a-b) / a(1-0·015b)
[C1 = 100(a-b) / a]
CHART FOR
OBTAINING
PERCENTAGE CONVERSION
F.D.M.

FIG. 42.

This is a much more convenient form than (2) because no term corresponding to *ab* is involved. As soon as the tests have been made the conversion may be obtained without reference to the dioxide content of either gas, either by calculation, or by reference to the alignment chart of Fig. 41. This chart is adapted to cover the greater part of the field which is needed in practice. It gives at a glance the percentage of dioxide in either gas, with a precision sufficient for many purposes; and on the application of a fine stretched thread or a transparent celluloid ruler, shows the percentage conversion on the central support.[1]

Method of Oxygen Estimation (2)—There are cases in which the method described is inapplicable, the principal being that of the Mannheim plant. In this plant the hot gas passes immediately from the pyrites kilns to the ferric oxide contact shafts. It is subject to great fluctuations in composition and a true sample is difficult to obtain. The temperature is so high that the sample is apt to undergo conversion in being drawn out. Each unit of plant consists of four kilns and oxide shafts, so that the difficulty of obtaining representative samples of the burner-gas for a whole unit is practically insuperable. In these circumstances the conversion can be obtained by indirect means with a precision which exceeds that of the usual direct test.

The gas sample is taken from the plant after the trioxide has been absorbed at either the first or second stage, and is drawn into a dilute solution of sodium hydroxide by means of an aspirator arranged to run for a number of hours. When the required volume of water has run out the sulphur dioxide absorbed in the solution is estimated, and also the oxygen in the residual gas in the aspirator. The usual defect of these continuous tests is that a considerable fraction of the sulphite is oxidised by the oxygen in the gas. It has been shown, however,[2] that if 5 per cent. of glycerine is added to the solution

[1] *Note on Construction of Fig.* 41.—M and N are set out to uniform scales on the parallel axes. The support for *c* passes, if produced, through the points (N, 0·5) and (M, 6). The graduations of *c* are obtained by projecting those of M on to the support, in the following way. Take, *e.g.* (N, 1000·5) as radiant. Then the projection of (M, 105) gives (*c*, 99·0); (M, 205) gives (*c*, 98·0) and so on. The gas-percentages may be added also by homographic projection from a uniform scale.

[2] Haller, *J. Soc. Chem. Ind.*, 1919, 38, 52.

before beginning the test, the passage of the oxygen, even at fairly high temperatures, has little effect. The estimation of the sulphite is best made by titration with standard potassium iodate, in a solution containing hydrochloric acid. The percentage of oxygen is usually found by absorption in alkaline pyrogallol in an Orsat apparatus.

Calculation of Results.—Suppose that a per cent. of sulphur dioxide and d per cent. of oxygen are found in the gas drawn from the plant, the *fractional* conversion being c. In the case of pyrites, to produce 1 vol. of dioxide by combustion, r vols. of oxygen will be required, r being greater than unity. Consider the a vols. of dioxide remaining. They are all which are left of $\frac{a}{1-c}$ vols., $\frac{ac}{1-c}$ having been converted and removed. The oxygen necessary to produce this dioxide is $\frac{ar}{1-c}$ and that necessary for conversion $\frac{ac/2}{1-c}$, so that originally the ratio of oxygen to nitrogen in the air consumed, must have been, if we include the d vols. which still remain—

$$\frac{d + \frac{ar + ac/2}{1-c}}{100 - a - d} \quad \frac{20.9}{79.1} = 0.264.$$

Solving this for c we find that the percentage conversion—

$$c = 1 - \frac{a(r + 0.5)}{26.42 - 1.264d + 0.236a}$$

The doubtful point lies in the choice of a value for r. According to the equation—

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2,$$

r should be $\frac{11}{8}$ or 1·375. Pyrites, however, is not a pure mineral and undergoes more than one chemical change on burning. To some extent incompleteness of burning and formation of sulphates in the cinder compensate one another. We have no data for evaluating r at present. For fairly pure ores 1·375 is probably not far wrong. The equation given, with this value, becomes for the percentage conversion:—

$$\frac{C}{100} = 1 - \frac{1.48a}{20.9 + 0.186a - d}$$

This method of calculation [1] was used at Queen's Ferry and was found to give results which corresponded closely with the known production of the plant. Series of tests of the burner-gas which were specially made showed that the equation could be relied on. The figures the equation yields are more in accordance with facts than those obtained by any other method of estimation which can be carried out under technical conditions.

The quantities a and d having been found, reference to the chart of Fig. 43 [2] gives the conversion at once. The chart may be used for either total conversion, or for conversion by the oxide shaft. The precision of the chart is probably rather higher than that of the method as a whole.

[1] It was introduced by H. V. S. Knibbs.

[2] *Construction of the Chart* (Fig. 43).—Set off a and d to any convenient uniform scales. Take any convenient length along the a axis and divide into 100 parts, numbering from 0 to 100 downwards, to form an auxiliary scale. Join $(a, 0)$ and $(d, 20{\cdot}9)$ to obtain the c support. Calculate a few values of c, *e.g.*, take $d = 10{\cdot}0$, then for $a = 2{\cdot}29$, $c = 70$; for $a = 3{\cdot}09$, $c = 60$; for $a = 3{\cdot}92$, $c = 50$, and so on. A few c values are thus located on the support. Now draw lines through these points (c) and the corresponding points on the auxiliary scale on the a axis. This gives a radiant point from which all the auxiliary values are projected on to the c support.

Thermal Data concerning Conversion and Preheating.

No.	Quantity.	Kilocalories per gram-mol.	Referred to.	C.H.U. per lb., or cals. per gram.
(1)	Heat of formation of sulphur trioxide at 18° [1]	22·6	SO_2	353
	$SO_2 + O \longrightarrow SO_3$ (gas)	...	SO_3	281
(2)	Heat of combustion of pyrites [2]	186·5	S	2915
	FeS_2	...	SO_2	1400
(3)	Heat of combustion of sulphur (S) [3]	69·3	S	2170
			SO_2	1085
(4)	Sulphur dioxide. Specific heat (*Cp.*).			
	" " " " 0°-200° [4]	9·89	...	0·154
	" " " " estimated for higher temperatures	$6{\cdot}5 + 0{\cdot}009\ (t + 273)°$	...	$0{\cdot}102 + 0{\cdot}00014\ (t + 273)°$
	Sulphur dioxide. Probable value about 450°	...	...	0·20
(5)	Sulphur trioxide (estimated value of *Cp.*—specific heat at 100°) [5]	12·6	...	0·16
(6)	Air. Specific heat (*Cp.*) [6]			
	" " " 20°-440°	...	...	0·237
	" " " 20°-630°	...	...	0·243
	" " " 20°-800°	...	...	0·243
	" " " 440°-630°	...	...	0·262
(7)	Burner-gas, 5-10 per cent. at about 450°	...	...	0·25

[1] Berthelot. According to Bodenstein and Pohl's results (q.v.) the heat of formation at constant pressure falls about 100 for each rise of 100°, but the values deduced from their results at 500°-700° are *higher* than Berthelot's at 18°, so the correction of the value given above to higher temperature would be valueless. See also p. 31 for Thomsen's value, etc.

[2] Sommermeier, *J. Amer. Chem. Soc.*, 1904, **26**, 555.

[3] Berthelot, see also p. 31.

[4] Regnault.

[5] Bodenstein and Pohl.

[6] Holborn and Austin.

CHAPTER VI

GAS-PURIFICATION

Catalyst Poisons.

The subject of catalyst poisoning has already been dealt with very briefly in connection with the theory and phenomena of catalysis, and it has been seen that we are as yet without any established explanation of the way in which these poisons act. The most detrimental and the most difficult to remove is arsenic. Its action is permanent. It is possible roughly to divide the known poison into two classes. In the first class of permanent poisons may be placed (1) arsenic, selenium, tellurium, and probably antimony; in the second or transient class (2) chlorine, hydrochloric acid, and probably iodine and silicon fluoride. In addition, a third class of substances must be included which, although they have no specific action on the platinum, are capable of hindering its action by forming a mechanical coating, or conveying to it mechanically a true poisoning agent such as arsenic. In this class (3) are elementary sulphur, oxides of bismuth, lead, iron, zinc, and other metals, lead sulphate, and various other salts and oxides. Silicon fluoride, by virtue of its covering the catalyst with a film of silica, may also be included. Only in case of very inefficient purification could such substances as lead sulphate reach the converters.

Arsenic.—It is a matter of fundamental importance to know how the arsenic from pyrites burner-gas is conveyed to the mass, and the methods by which this gas can be purified from it. Success is otherwise impossible. The claim to have discovered the great importance of the compounds of this element has been the subject of a polemical discussion which now has little interest. On the one hand it was contended that

Clemens Winkler was well aware of their injurious effect,[1] while on the other the *Badische* Company claimed that Knietsch and his co-workers first realised the necessity of removing such impurities. However this may be, we possess in the lecture which was given by Knietsch[2] the first account of investigations made along this line, which, although more than twenty years have elapsed since its utterance, still possesses a cogent interest.

The first experiments were made in the laboratory with actual burner-gas which was taken in through a long lead pipe which acted as a dust-remover. The gas was washed with concentrated sulphuric acid and passed over the contact-mass. The results were almost as complete as those obtained with artificial mixtures of gases, and no falling off in the quantitative action was observed, although the experiments with the same contact-mass lasted several days.

This seemed to justify the hope that sulphuric acid might be made almost quantitatively in this way from burner-gas, and the experiments were repeated on the large scale; but it was soon found that the action of the contact-substance did not hold out during prolonged use, and ultimately failed entirely. This result was not improved by cooling the gas in long flues and repeatedly washing it with sulphuric acid, nor by filtering it through dry coke and asbestos filters so that it might be regarded as pure as could then be technically attained. The large scale experiments had therefore to be regarded as failures.

Confidence in success was disturbed by these unexpected results, but further laboratory experiments were made to find the reason of this slow and apparently inevitable loss of activity. The surprising discovery was then made that some substances interfere with the catalytic action even when present in minute quantities. Arsenious oxide takes the first place in this class and other oxides which at first were thought to be specifically harmful, for instance those of mercury and phosphorus, were later found to act as arsenic carriers. The injurious effect of arsenic was found to be so great that 1 to 2 per cent. in the contact-mass deprived it of activity entirely.

[1] *Z. angew. Chem.*, 1905, 1655 and 1902.

[2] *Ber.*, 1901, 84, 4069.

The question now arose—were these contact poisons actually present in the burner-gas after the performance of all the purifying operations described? It was found in answer that the white mist of sulphuric acid which had not been completely precipitated did, in fact, contain arsenic. A reason for failure was therefore defined but no means to success were immediately to hand, for the technical science of the time had found no way of completely precipitating these mists, or of causing them to settle.

The task was accordingly taken in hand once more, this time with the object of removing impurities *completely*. The rocks on which the earlier workers had been wrecked were now accurately charted and the course lay clear. Experiment after experiment was made, expensive in time, money, labour, and patience. Each mistake was followed by a lasting diminution of the yield of the whole plant, but at last this most difficult problem was solved. The final result was that the burner-gas could be freed from all impurities if, after suitable treatment and cooling, it was subjected to continued systematic washing with water or sulphuric acid, carried out until optical and chemical examinations gave satisfactory results. The intimate contact of the gas with the purifying liquids could be secured by vigorous washing, or wet filtration, or a combination of both.

It was found to be advisable to cool the gas slowly, for the mist was much more readily precipitated under these conditions than when rapidly cooled. For this cooling, long iron conduits were employed, and it was at first thought that iron could have no injurious effect for sulphuric acid of more than 90 per cent., such as is formed when pyrites is burnt, was not expected to have any action on iron, or at most to liberate some sulphur dioxide. But although the burner-gas was completely free from impurities which the optical test could detect, and for greater security had been further purified by filtering through wet filters constructed like ordinary filter presses, the result was again a very slow but certain decrease of catalytic activity, extending over months. A long series of investigations was made, and only after the presence of arsenic, indiscoverable in the gas, had been proved in the deteriorated platinum contact-mass, did the assumption gain

ground that the disturbance arose from the action of the acid condensate in the cooling pipes, resulting in the generation of a gas containing arsenic, probably arseniuretted hydrogen. Precautions were then taken to prevent the condensed acid from coming into contact with iron, and from that time the contacts continued to function without loss of activity.

On carrying out the process on a still larger scale, another cause of disturbance appeared. When the pyrites-burners were worked to their fullest extent, mist appeared which was precipitated only with the greatest difficulty and was found to consist of minute particles of unburnt sulphur. This sulphur contained arsenic which, on account of the more intractable nature of the sulphur mist, was apt to reach the contact-mass unaffected. The only remedy was to provide for such an intimate mixing of the burner-gas that the combustion of the last traces of sulphur was assured. To this end a blast of steam was introduced. This was effective, had other advantages also, and became a distinguishing feature of the *Badische* system of gas purification.

It would be an error to suppose that plant experiments of this nature were confined to the works of the *Badische* Company, for it appears that at the time investigations were proceeding in most of the large German works, and elsewhere. The delivery of Knietsch's lecture in 1901 gave a deserved prominence to the *Badische* results.

Compounds of Arsenic.—Of the several ways by which arsenical compounds may be supposed to reach the contact and poison it, the first mentioned—transport in the sulphuric acid mist—is the most important. Purification of the burner-gas from arsenic means elimination of the mist. The second method of transference—as arsenious hydride—is by no means so clearly established. So far as can be ascertained it has never been shown, by experiments made to test this point solely, that arsenious hydride is generated from concentrated sulphuric acid, arsenical flue-dust and iron, and in regard to its action on platinum contact-mass we have no specific data. But it is nevertheless considered bad practice to have any iron or steel in the plant in such a situation and at such a temperature that acid may condense on it from gas which has not been completely purified. Iron pipes have often to

be used for conveying the burner-gas from the dust chambers to the gas-coolers but these are often lined with firebrick, and the metal here, as well as in the fittings of the furnace and dust chambers, is at so high a temperature that no arsenious hydride can exist even if it were formed.

It is not likely that the hydride is the actual poisoning agent, for in presence of the great excess of oxygen arsenious oxide is probably formed on approaching the contact-mass. There is no definite information on the point so far as small concentrations of hydride are concerned. Neither is it quite certain what action, if any, concentrated sulphuric acid has on traces of the hydride. It is stated that concentrated acid at 160° to 180° causes partial decomposition,[1] but on the other hand that hydrogen containing small amounts of the hydride can be dried over the acid without change.[2] It may be added that water, or dilute sodium or potassium hydroxide has no marked power of absorbing the pure gas.

There is also a third possibility. The vapour of arsenious oxide may pass through, although all the solid oxide and all mist have been eliminated. The vapour pressure of this substance is extremely low, and is hardly measurable with precision by the ordinary methods at atmospheric temperatures.[3] Some determinations made by passing air over the pure substance and estimating the amount carried away gave the following approximate values:—

Temperature.	60°,	83°,	103°,	124°,	142°,	150°
V.P. in mm. of mercury	$2{\cdot}4\times10^{-7}$,	$2{\cdot}5\times10^{-5}$,	$4{\cdot}6\times10^{-4}$,	$2{\cdot}2\times10^{-3}$,	$1{\cdot}4\times10^{-2}$,	$2{\cdot}6\times10^{-2}$

By a similar method the vapour pressure of arsenious oxide dissolved in concentrated sulphuric acid to the extent of 0·015 per cent. was found to be about 4×10^{-7} mm. at 60°.[4] Supposing that acid of the same composition is being used in a scrubber or drying-tower, at the same temperature, it can be calculated that the weight of arsenic removed as vapour will be about 10^{-6} gm. in every cubic metre of gas. It seems extremely improbable that an impurity in such a minute concentration could have any effect.

[1] Forbes, *Chem. News*, **64**, 235.
[2] *Gmelin Kraut*, **3**[ii], 1908, 435.
[3] It amounts to 13-14 mm. at 563°. Gmelin Kraut, **3**[ii], 1908, 442.
[4] Smellie, *J. Soc. Chem. Ind.* (*Trans.*) 1923, **42**, 467.

Some data for the solubility of arsenious oxide in sulphuric acid have been given by Braidy.[1] They have a certain bearing on the possible removal of arsenic by washing the gas with acid, and are given, in part, below—

Gms. As_2O_3 in 100 gms. acid at 17°	1·8	1·0	0·5	0·3	0·3	0·2	0·2	at 50°	0·7	0·5	0·4	0·3
Sp. gr. of acid	1·0	1·20	1·36	1·5	1·6	1·72	1·82		1·45	1·6	1·72	1·82

Special Methods of Arsenic Removal.—The best known proposal to provide special means of removing arsenic from the burner-gases is that embodied in the Mannheim process-passage through hot ferric oxide. There is no doubt that under favourable circumstances, with not too much arsenic in the ore, the greater part of it can be eliminated in this way, but the efficiency of the process is too low for any reliance whatever to be placed on it. If the ore is fairly arsenical the oxide shafts may retain from 90 to 95 per cent.; if it has a small arsenical content (0·1 per cent. or less) only 60 per cent. may be retained. In either case more passes than the somewhat elementary purification system of the usual Mannheim plant is able to deal with, and this is sufficient to poison the contacts. Anhydrous aluminium sulphate, obtained by heating the hydrated salt, is also said to retain most of this impurity (Projahn, Ger. P. 221847). Quicklime mixed with asbestos is often used in Mannheim filters and is said to be effective for some time. Slaked lime, calcium carbonate, or dolomite are mentioned also in a patent claiming their use (Du Pont, U.S. P. 989801). A more recent proposal of the Grasselli Company (U.S. P. 1103522) was that of improving the Mannheim process by introducing, after the usual filters, another filter packed with hydrated ferric (or copper) oxide, which is said to have the power of absorbing arsenious hydride. But it is fairly certain that no specific reagent, apart from a thorough purification from dust and mist, is of any use.

Removal of Arsenic from the Contact-Mass in situ.—The access of compounds of this element to the platinum results in a loss of activity which increases in proportion to the amount of arsenic present. To compensate for this to some

[1] *L'Ind. Chim.*, 1922, **9**, 45.

extent, the temperature of the mass can be raised; but this adjustment is of course limited in extent by the inevitable change in the equilibrium conditions, which results in diminished yield. In Mannheim plants where the poisoning of the mats is often constantly proceeding, the temperature of the contact chest has to be the higher the older the mats, and may rise in this way from 475° to 550°. In many Grillo plants burning pyrites this increase is also resorted to, so that of a number of plants there may hardly be two which are converting at the same temperature. These remarks do not, of course, apply to the same extent to plants with efficient systems for purification, where the mass may remain in constant use for many years without removal. Once thoroughly poisoned, asbestos contact-mass can be utilised only for the recovery of the platinum. This applies also to Grillo mass, when the deterioration is sufficiently advanced.

There are, however, certain methods which have been proposed for treating the contaminated mass in the converter, and removing the arsenic without destruction of the material. A patent of the Höchst works (Ger. P. 135887 of 1902) claims that platinum mass poisoned by arsenic can be regenerated by mixing steam with the hot gas entering the apparatus. The admixture of steam is continued until no more arsenic can be detected in the condensate from the converter. Another patent taken out by the *Badische* (Ger. P. 148196) states that the same result is reached by merely using dry sulphur dioxide, either alone or mixed with gas containing little or no oxygen, at the temperature of conversion. The application of these two patents, if it is considerable at all, must be very limited. Grillo and Schröder (Ger. P. 115333) describe the removal of arsenic, antimony, or mercury from the contact-mass by the action of chlorine at the ordinary temperature of the contact space. Any oxides of these metals may be reduced to the metallic state by means of coal-gas. This method has occasionally been tried on various types of plant, chlorine being passed into the contact space and allowed to remain there for some time It should be noted that under these conditions platinum, like gold, may be lost by volatilisation as chloride.[1] Hydrochloric acid mixed with sulphur dioxide has also been used, and is said

[1] Reese, *J. Soc. Chem. Ind.*, 1903, 22, 351.

to be more efficient for the purpose.[1] In laboratory experiments made partly to test the efficacy of this, gas and chlorine, it was found that magnesium sulphate mass which was giving good conversion, was made completely inactive by allowing arsenious oxide to sublime on to it in the gas stream, from the front end of the reaction tube. Hydrochloric acid was then passed for fifty minutes, the temperature being maintained, and then air for fifteen minutes. Conversion after this treatment was 96.5 per cent. Chlorine was not so efficient, and platinum was found in the further end of the reaction tube.

In a more recent patent specification of Briggs and the General Chemical Company (U.S. P., 1429222, of 1920), instructions are given for revivifying asbestos contact-mass by washing out the whole converter with water. The contact chamber is cooled to about 30° C., and water at the ordinary temperature is run in at the bottom fast enough to dissolve soluble material without permanently displacing the mass. With a converter of the Herreshoff type, such as that described in U.S. P. 719333, but 7 feet in diameter, with 50 plates an inch apart, and mass occupying from a half to three-quarters of the space between the plates, the water may rise in the vessel 10 inches in an hour. The converter having been filled, the inflow at the bottom is closed, warm water at 25-30° is run in at the top and allowed to flow out at the bottom. When the runnings show no matter in solution the converter is emptied at the same rate as it was filled, and hot air is then passed in at the top less rapidly than the gas is normally supplied. The temperature of the entering air is raised until that of the contact-vessel is 450°, and the apparatus is then ready for use.

Selenium Tellurium.—These elements are present in some kinds of pyrites, and are particularly prevalent in Japanese sulphur, often together with arsenic. Selenium is a powerful contact poison, and appears to be conveyed to the catalyst as selenium dioxide by the sulphuric acid mist. Means of purification which are efficient for removal of arsenic appear to be sufficient for removal of selenium. Appropriate methods have been worked out for the detection and estimation of small amounts of selenium in either pyrites or sulphur.[2] Tellurium

[1] Reese, *loc. cit.* [2] Klason, *Z. angew. Chem.*, 1912, 25, 514.

is also an active poison, but little concerning its action is on record.

Hydrochloric Acid. — It is probable that any chlorine originally present in the pyrites or sulphur is evolved from the burners in the form of hydrochloric acid. The poisoning effect is temporary, and on passage of air or of pure burner-gas, the activity is fully restored. In some laboratory experiments[1] the introduction of a small proportion of hydrochloric acid caused a normal conversion to fall at once to 92 per cent. After passing air for thirty minutes and then burner-gas once more, conversion rose to 94 per cent., even while the exit-gas contained traces of hydrochloric acid. If sufficient chlorine is present in the gas entering the converter, conversion will fall in a very short time—under these conditions a test made by bubbling the inlet gas through acidified silver nitrate solution may show a heavy precipitate in a few minutes—and to recover conversion while the impurity is still coming through is not usually possible. Smaller quantities, however, produce a more moderate diminution in activity, which can, partially at least, be compensated for by raising the temperature of the mass. But if the regenerative system is complete, and the plant is run with the superheater cut out, the temperatures in the converter are likely to fall irrecoverably before the inlet temperature can be sufficiently raised. Nothing then remains but to remove the poison from the mass by passing air through it at 400° to 500°, and to begin again with gas free from the poison.

The efficiency of the purification system in regard to hydrochloric acid depends on the solubility of this gas in the purifying agents. If these agents consist of sulphuric acid, it is essential that in one instance at least this acid shall be sufficiently weak to absorb the gas. The solubilities of hydrochloric acid in sulphuric acid of several concentrations are given below for ordinary room temperature.[2] The

Per cent. H_2SO_4 in acid	20	40	50	70	80	90
Grams HCl dissolved by 100 c.c. acid	50	27	7	1·7	0·5	0·2

[1] Reese, *loc. cit.*

[2] Gretna Factory, E. Taberner, R. Hay, and A. J. Vale.

solubility is roughly in linear relation to the acid strength until 60 per cent. H_2SO_4 is reached. It then falls very rapidly.

Considerable trouble was experienced from the presence of hydrochloric acid in the burner-gases in H.M. Grillo plants during the War—partly on account of the contamination of sulphur by sea-water—and it was found necessary to maintain the washing acid in one of the scrubbers at about 50 per cent. In extreme cases even this was not sufficient, and water was

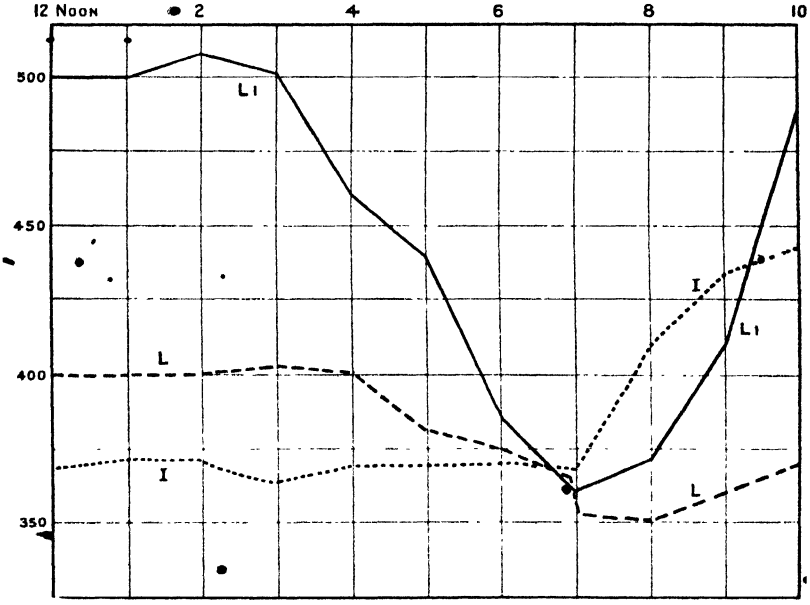


FIG. 44.—Graph showing effect of Chlorine Poisoning on Grillo Conversion-Temperatures.

sprayed into the burner-gas entering the gas-cooler. This worked well, but involved a certain loss due to the removal of sulphuric and sulphurous acid in a very dilute form. The effect of the access of hydrochloric acid on the normal working of a Grillo converter in an extreme case is shown in Fig. 44. I denotes the temperature of the inlet gas. This remains constant throughout until increased by throwing in the pre-heater. L denotes the temperature of the gas entering the first layer, after passing through the regenerating converter jacket, and L_1 the temperature leaving the first layer, which as in the usual working of the plant, was at that time performing

most of the work of conversion. At about 3 P.M. L_1 begins to fall rapidly, and at 6.45 P.M. no conversion is taking place at all. Meanwhile the scrubbing acid has been reduced in strength and the preheater thrown in and fired. The result is shown in the rising temperatures. At 9 P.M. conversion had partially recovered, to 90·7 per cent. (Gretna, 17th July 1919).

Washing with sulphuric acid of 50 per cent. H_2SO_4 is not a very efficient means of purification, as the very small concentration of hydrochloric acid corresponding to the partial pressure of this gas in the gas-mixture is soon reached, and then the washing acid must be renewed. Washing with water, or with the dilute alkaline solution employed in the Tentelew method of purification is much more efficient, and this is one of the reasons why that method has been adopted on some plants which, apart from purification of the gases, have not very much in common with the Tentelew design.

Sulphuric Acid Mist.

The formation of "chemical" mists is an interesting subject, and the astonishing permanence they may show has never been satisfactorily explained. In each of the cases which have been investigated the mist has been found to be formed by a reaction between two or more substances in the state of vapour. Ammonium chloride and phosphoric acid are familiar instances; others are found in the fogs (probably of iodic acid) caused by the passage of ozone through the aqueous solution of a reducing agent which is acid or neutral. Sulphuric acid is technically the most important instance. Air containing any one of these four mists can be passed several times through water without complete purification resulting. Ammonium chloride is distinguished from the others by being anhydrous in the state of fume, and this fact, as will be seen shortly, has a bearing on the case of sulphuric acid also.

In the Contact Process the burner-gas always issues from the burners at so high a temperature that little or no sulphuric acid (H_2SO_4) can be present in it, for vapour density measurements show that at 440° this compound is dissociated almost

entirely into sulphur trioxide and water. Below the temperature our knowledge of the system sulphur trioxide-water is very scanty and uncertain, and we are unable to say whether the principal phenomena which occurs as the gas-mixture cools is the combination of the two vapours to form *liquid* sulphuric acid, or the formation of sulphuric acid vapour and its subsequent condensation. It is doubtful, indeed, whether sulphuric acid at temperatures above 200° can exert any considerable vapour pressure other than that of the resultants of its dissociation. The measurements of Burt[1] showed that up to 200° the observed tensions were due in all probability to water only. More recently, on the other hand, Thomas and Ramsay[2] have reported that sulphuric acid exerts a partial pressure of H_2SO_4 which even at 140° is 0·23 mm. (for 97·6 per cent. acid). At 200° it is 2·7 mm. and at 261°, 22·4 mm. These results will be of great value if the confirmation is forthcoming which the great difficulty of the determinations demands.

In regard to the physical basis of the mist formation we are almost as much in the dark. Condensation may occur on solid particles of dust, or on gas molecules which have been ionised by passage through the furnaces. Knietsch's statement that slow cooling is advisable, runs parallel with the assumption that the more quickly the gas is cooled the smaller will the particles tend to be. As the temperature falls to that of the purification process, the acid in the globules tends to become diluted by taking up water from the surrounding gas.

It is the salient fact in connection with sulphuric acid mist that this dilution does not occur nearly as rapidly as might be expected. Matter in fine division has unusual (colloidal) properties and, as Lord Kelvin showed, the vapour tension of a small spherical liquid drop is greater than that of the normal liquid, in inverse proportion to its radius. If, then, the droplets of acid (which we may suppose slightly diluted during the cooling) are very small, their increase of vapour tension due to curvature may be so great that this tension is equal, or nearly equal, to that of the water or weaker acid with which they are being washed or scrubbed. In these circumstances the washing process will necessarily be slow,

[1] *J. Chem. Soc. Trans.*, 1904, 85, 1339.

[2] *J. Chem. Soc. Trans.*, 1923, 123, 3256.

and will depend greatly on the vigour of the mechanical agitation of gas and liquid.

This view of the matter (first taken, in a general way, by Townsend)[1] is in fair accordance with the facts, and receives support from some experiments made by Rothmund on the fogs developed during the reduction of ozone.[2] The diameter of these particles was evaluated in two ways. The first consisted in observing their rate of fall, and deducing the diameter from this rate and other data, by Stokes's law. The second involved the assumption that the particles were really in equilibrium as regards water vapour with the surrounding gas. Both methods gave results of the same order, the mean of which was about $1{\cdot}0 \times 10^{-4}$ cm. Similar values, ranging from 1×10^{-3} to 1×10^{-4} cm., were obtained by Delasalle for sulphuric acid mist from concentrators.[3]

Sulphuric acid and ammonium chloride mists have been investigated by Remy[4] with most suggestive results. Air containing the mists was passed through the absorption wash-bottles and into a cylinder at the bottom of which lay "conductivity" water. After allowing the particles to settle in the cylinder, the amount of substance unabsorbed was obtained by a conductivity measurement. It was found that in every case the absorption of ammonium chloride in the wash-bottles was more rapid in water than in a nearly saturated solution of that salt. If now the chloride fume was replaced by that obtained by blowing damp air over oleum an apparent contradiction appeared, for the absorption in water was visibly incomplete, whereas the gas passing away from the washing with 98 per cent. acid was seen to be quite clear. The conductivity measurements, however, showed that the absorption in water was really the greater. The 98 per cent. acid was the worse absorbent, but rendered the mist invisible, and on passing the gas into water once more, the fog reappeared. It is clear that such facts are of great interest in regard to the scrubbing of burner-gas with sulphuric acid. The statements sometimes made that 98 per cent. acid is effective for mist removal seem to rest, at least in part, on a confusion between sulphuric acid mist and

[1] *Proc. Camb. Phil. Soc.*, 1900, **10**, 52. [2] *Zeit. Elektrochem.*, 1917, **23**, 170.
[3] *Chim. et Ind.*, 1920, **4**, 291. [4] *Zeit. Elektrochem.*, 1922, **28**, 467.

sulphur trioxide. To absorb the vapour of the latter substance, 98 per cent. acid is of course, essential and it is interesting to note in passing that Remy found concentrated ammonium chloride solution was more effective than water in the absorption of the fume made by subliming the carefully dried salt.

The stability of sulphuric acid mist has often been a subject of comment. It is probable that in addition to the effect of the curvature of the droplets on their surface tension, the presence of electric charges may exert an effect, in a direction opposite to the first, and comparable with it in the case of very small droplets.[1] An attempt has been made by Bancroft and others to explain the permanence of the mist by the assumption of a film of adsorbed air on the surface of the particles.[2] It is supposed that many other phenomena can be explained in the same way; the rebounding of two water drops from each other and the fluidity of certain powders such as zinc oxide are instances. The air-film theory seems to rest on little positive evidence and so far as its application to solids is concerned, has received severe criticism.[3]

The amount of the sulphuric acid which has to be removed from the burner-gases depends entirely on the rate of formation of trioxide in the burners. Even when pure sulphur is burned in air, from 2 to 3 per cent. of trioxide is formed and this figure, if the sulphur is of poor quality and produces much dust, or if the brickwork of the furnaces is high in iron, may be raised to 5 per cent. The conversion in pyrites burners is in general higher, and is often found to be between 5 and 7 per cent., and in special cases even more. For further information the volume of this work dealing with the Chamber Process may be consulted.

If we pass to the sulphuric acid which is formed when the mist is precipitated, we find that the composition of this acid, the temperature, and the amount of aqueous vapour in the gas from which the acid has been precipitated are closely connected in a way which, roughly at least, can be calculated. The higher the temperature of precipitation from a gas mixture of

[1] For mists in general, see *Clouds and Smokes*, Gibbs, 1924.

[2] *Applied Colloid Chemistry*, Bancroft, 1920, 21.

[3] *Edser, 4th Report on Industrial Colloid Chemistry, Dept. of Scient and Ind. Research*, 1922, 271.

given composition, the higher is the concentration of the acid formed. In a plant burning sulphur, 5·1 per cent of which was converted to trioxide in the burners (an unusually large amount), the burner-gases entered the lead-pipe gas-coolers at 285°. The strengths of the acid condensed in the several pipes as the temperature of the gas fell was: No. 1, 92·1; 2, 79·8; 3, 74·7; 4, 72·0; 5, 71·7; 7, 70·8; 9, 65·2 per cent. In the case of a large filter or scrubber, in which the gas mixture is exposed to intimate contact with the deposited acid, the amount of aqueous vapour in the gas leaving the apparatus (as distinct from water in the sulphuric acid mist still remaining) will not be very different from that calculated from the vapour pressure of the acid with which the apparatus is filled. In the case of a large gas-filter, the effluent had been fairly constant in composition for many days (58 per cent. H_2SO_4). The average internal temperature was 13°. In Sorel's tables of vapour pressure 2·3 mm. is given for 58 per cent. acid at 13°. If the water vapour (w) is measured in milligrams per 100 litres, and the vapour pressure of the liquid (v) in mm. of mercury, the relation enables w to be calculated as:—

$$w = \frac{28900v}{t^\circ + 273}$$

In the present instance it is about 230. A series of direct tests made on several consecutive days, by a method outlined below, gave 310 mgm. of water and 70 mgm. H_2SO_4 as the two constituents of the mist and water vapour. The second figure for the water is naturally the higher, on account of some water being associated with H_2SO_4 in the liquid condition. It is only under very constant conditions, however, that such calculation is of real value for the working of any part of a plant.

The strength of the acid deposited in the filters and in other parts of the plant, is dependent on the relative amounts of water and sulphuric acid which issue from the burners. Three factors influence it: (1) The burner conversion; (2) the humidity of the atmosphere; (3) the moisture in the ore or sulphur. In many cases the burner-conversion under ordinary conditions is known, or can be estimated by determining the

strengths and amounts of the acid removed in purification. The atmospheric humidity can be found from readings of the wet and dry bulb hygrometer, and the usual tables. But for calculations of any precision this method should be avoided, for so much depends on the precise nature of the conditions under which the wet bulb is exposed, and much more reliable results are obtained by the positive method of aspirating the air through tubes containing sulphuric acid and phosphorus pentoxide, and weighing the tubes.

Suppose that the pyrites-burner conversion is 7 per cent. and a 7 per cent. gas mixture results (as estimated by the usual test in the cold). In 100 litres of gas there are $7 \times 7/93 \times 80/22{\cdot}4$ gm. of trioxide in the liquid condition, or 1·88 gm. The air necessary to produce this 100 litres of gas, if we make the same assumption as on p. 193, and neglect the formation of the small amount of trioxide, is $100 + (7 \times \frac{3}{8})$, or about 103 litres. If, as may happen often in summer, 100 litres of air contain 1·00 gm. of water (corresponding to saturation at 11·2°), the H_2O present = 1·03 gm., and, as has already been seen, the ratio of SO_3 to H_2O must be at least a little higher in the acid which is deposited than in the aggregate of SO_3 and H_2O in the burner-gas, on account of some of the water being present as vapour. The deposited acid must, therefore, contain rather more than $1{\cdot}88 \times 100/(1{\cdot}03 + 1{\cdot}88)$ per cent. SO_3, or 79 per cent. H_2SO_4. But under winter conditions the humidity will not be so high. Suppose it to fall to 0·6 gm. per 100 litres (saturation at 0·3°). The water drawn in is then approximately half the former amount, and the deposited acid must contain rather more than $1{\cdot}88 \times 100/(0{\cdot}62 + 1{\cdot}88)$ per cent. SO_3, or 92 per cent. H_2SO_4.

Tests for Gas Purification.—If the purification is incomplete more or less sulphuric acid will condense in the blower and the subsequent parts of the plant. One very general method of controlling readily the completeness of purification is to use the optical test. The purified gas is caused to pass through a pipe 10 or 15 yards in length, the ends of which are fitted with glass windows. The purity can be estimated by the clearness with which an object with a sharp edge can be viewed through both windows, a lamp being used at night to illuminate the edge. In some cases observation windows are fitted to the

upper parts of the gas-filters of plants. These permit of the observation of the gas as it actually emerges from the filtering material, and if a powerful lamp with a lens is used, a beam may be thrown into the gas space, and the Tyndall effect observed. Such fixed windows are apt in time to become clouded with deposited acid and other dirt, and cannot, like the observation tube, be cleaned while the plant is in action.

Tests are frequently made of the "total moisture," that is, of sulphuric acid mist together with aqueous vapour (and other possible impurities) in the purified gases, by aspirating samples through tubes packed with phosphorus pentoxide and asbestos or glass wool. The double stoppered tube shown in Fig. 45 (*a*) is useful for this purpose and is very readily filled and cleaned out. A modification sometimes made is to pack the first tube with cotton-wool to absorb the acid mist more completely, and the second with phosphorus pentoxide. As large a volume of gas as practicable must be aspirated, for the quantity to be weighed may be only a few milligrams per 100 litres.

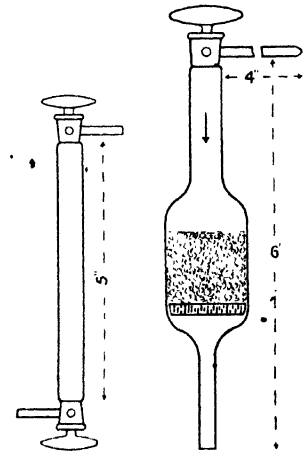


FIG. 45.

It is often desirable to estimate the total moisture in the gases at various of the earlier stages of the purification. If the total moisture is not very high, say less than 300 mgm. per 100 litres, this is not beyond the scope of the method just given, or of a slight extension of it; but when greater amounts of moisture and a correspondingly greater amount of acid mist is present, difficulty in withdrawing a sample is encountered and the results are apt to be irregular and unreliable. Consistent results can sometimes be obtained by placing the drawn-out end of the inlet tube just inside a short branch-pipe (about 1 in. long) sealed into the main pipe from which the sample is with-

drawn. It is also sometimes useful to be able to discriminate between the water and the sulphuric acid which make up the total moisture and, subject to the limitations regarding sampling, the piece of apparatus illustrated above (Fig. 45 (*b*)) has been found well adapted for the purpose. A small Gooch crucible filter-plate is placed in the tube before the end is drawn out. On this is built, before a test, a plug of moist filter paper, made by shaking up the paper with water in a flask and pouring the pulp into the tube, suction being applied by a filter-pump. The pad is partially dried by aspirating air through it, and is then connected to a tube like that of Fig. 45, packed with anhydrous calcium chloride and to a third similar tube containing phosphorus pentoxide. After the test has run, the gas in the tubes is replaced by dried air which is slowly aspirated through. The gain in weight gives the total moisture. The sulphuric acid is caught in the paper pad to the extent of 94 or 95 per cent., and can be estimated by pouring warm water through the tube and titrating the solution so obtained, careful attention being given to the inlet tube. The thickness of the pad should be about $1\frac{1}{2}$ in. If the acid mist consists of concentrated acid, the paper may readily char, and in that case can be replaced by a pad of asbestos of the kind used in Gooch crucibles, about $\frac{3}{16}$ in. thick. If representative gas samples can be taken, the method gives useful comparative results, when the amount of mist or moisture is not too low.

Methods of Gas Purification.

The operations of gas purification, although differing greatly from one process to another, must all have the same ends in view—the removal of solids, liquid and gaseous substances from the mixture of sulphur dioxide, oxygen, and nitrogen. First of all the furnace dust has to be precipitated as far as possible, and then by filtering or scrubbing the mist and other impurities must be dealt with. Finally, the gases must be dried, for although water vapour in small amount shows little specific action on the catalytic reaction for some time, its presence would cause sulphuric acid to be present in all the plant subsequent to the converter—which alone

would be very undesirable. The means of gas purification may therefore be divided into five branches:—

(1) Dust-removal.
(2) Cooling.
(3) Filtering.
(4) Scrubbing.
(5) Drying, and also (6) Special means of purification.

Each of these will be discussed in turn. In the latter part of this volume will be found descriptions of the construction and working of several types of complete plant, which have been found effective in practice. From time to time reference to this part will be indicated.

Dust Removal.

The raw materials used for the manufacture of oleum are (with unimportant exceptions) pyrites and sulphur. In burning pyrites a considerable amount of solid dust is carried away from the burners, especially when these are of the mechanical type and this, reaching the cooler parts of the plant, forms with the condensed acid a thick sludge which impedes the working of the plant. Sulphur naturally gives far less dust, but means are nevertheless provided for catching what is formed.

The removal of dust from the gases of the burners of contact plants does not differ in any essential respect from the same operation in the case of a chamber plant, and for more detailed information reference may be made to the appropriate volume of this work. Dust chambers are always placed after or on top of the burners, and generally consist of brick chambers, lined with firebrick, of as large area and volume as possible. Iron baffle-walls are sometimes built in the chambers at right angles to the direction taken by the gas stream, in order that the dust which falls to the floor may not be swept forward in the current. The Howard dust-settler is in use on many plants, and was observed to be part of the Höchst installation, with twelve Wedge furnaces, each taking about 21 tons of ore a day, about 1919. It is frequently fitted to Tentelew plants.

In contact plants the construction of the dust-chamber will be conditioned to some extent by the desirability of utilising

waste heat from the burner-gases. If the cold gas is to be preheated by means of the burner-gas, the dust chamber and preheater may be combined. If the heat is not to be utilised, the dust-chamber may be constructed in iron or steel. Whatever the construction, there is little chance of acid condensing on iron, for the prevailing temperature is usually well above the limit required. In general the gases should leave the dust-chamber at 275° or higher. In some plants this temperature is much exceeded.

Electrical Precipitation of Dust.—In recent years the Cottrell process has been applied with great success to cleansing the gas from the pyrites-burners of oleum plants. It consists essentially in the precipitation of the particles on earthed positive electrodes, in the form of plates or tubes, by means of high-tension discharge from negative electrodes in the form of plates or rods. A voltage of 30,000 or more is required. This development has been worked out in Germany and in the United States. In the latter country isolated installations were put in as far back as 1916. For some time past a precipitator has been in operation cleaning the gas from mechanical furnaces burning roughly 70 tons of pyrites each twenty-four hours, with an efficiency of 98 per cent. About 6 tons of dust is recovered in a week, a large part of which would have gone forward, under ordinary conditions, to block up the coolers and washers. The temperature of the gas treated is 500° and the power consumption of the plant only 3 kilowatts. The results of this installation were so convincing that the battery of Howard dust catchers was replaced by electrical precipitators.[1] Work on these lines was put in hand in Germany as soon as the War broke out, and proved very successful. The dust-laden pyrites gas was found particularly well-conditioned for electrical treatment. The design is of the plate and wire type, free from unnecessary complications and reasonably inexpensive (Fig. 46). To guard against dust passing through and causing stoppages in case of failure of the current, a system of automatic control and alarm gear was used; but such precautions were found in practice to be less important, as the operation proceeded with hardly any interruption except for the removal

[1] Bush, *J. Soc. Chem. Ind.* (*Trans.*), 1922, 41, 22.

of the accumulated dust. The controls were therefore simplified, and instead of having one compartment standing idle, twin compartments were used, of such a capacity that one could handle all the gas at a reduced efficiency, while the other was cut out for cleaning. More than twenty plants were installed during the War in connection with oleum

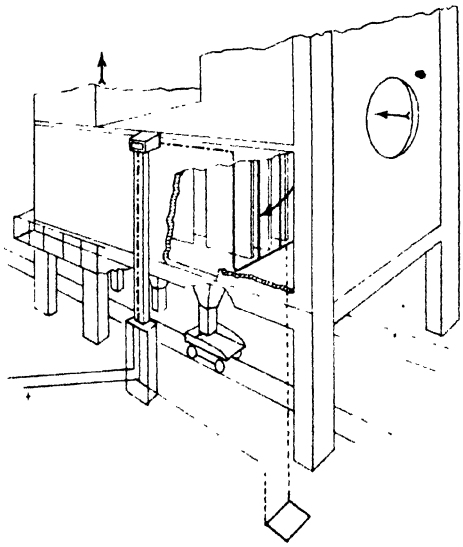


FIG. 46.—Electrostatic Dust-Separator.

manufacture at the works of the *Griesheim-Elektron*, Bäyer (Leverkusen), Nobel, Von Heyden, and at Uetikon in Switzerland.[1]

At the Bäyer works, where soon after the War from 80 to 100 tons of sulphur trioxide were being made daily from pyrites containing 40 per cent. of sulphur and a certain amount of zinc, the fines from the crushers were burnt in mechanical roasters of the M'Dougall type containing five or six hearths, and in one Wedge roasting furnace of large capacity. The hot burner-gas was led into a brick dust collector where the heavier particles of dust could settle, and then passed, by means of an air-cooled stack, into a second dust-chamber where still further amounts were removed. Finally the very fine dust was removed

[1] Bush; *loc. cit.*

by passage through a brick chamber containing horizontal iron plates spaced less than an inch apart. The lump ore was burnt in lump burners of standard design, and the gas passed through a dust collector, cooling stack, a second dust chamber, and finally through an electrical precipitator consisting of iron grids and iron wires suspended in a brick flue and separated by porcelain insulators. A difference of 70,000 volts was said to be maintained. The arrangement for cleaning, consisting of the division of the separator into two units, has already been mentioned. The two chambers together disposed of about 160,000 cb.m. of gas in twenty-four hours, corresponding roughly to a time of fifteen to twenty seconds in the flue, and a linear velocity of 25 to 30 ft. per minute. The efficiency of such plants built during the War was from 97 to 99·5 per cent.

A very interesting account of experimental work carried out by the *Service des Poudres* in France during the War, in connection with both pyrites-burners and Gaillard towers, has been given by Delasalle.[1] The experimental dust precipitator connected to one of the pyrites-burners of an oleum plant is shown in Fig. 47. The positive (earthed) electrodes were twelve iron pipes 0·28 metre in diameter and 3 metres long. These pipes were suspended in two perforated iron plates, so that the gas from the furnace was compelled to pass upwards through them. The negative electrodes were of galvanised steel rod of 10 to 20 mm. diameter, and were suspended from a horizontal metal bar which rested on the terminal insulators. The ends of this bar projected through two holes in the outside walls of the precipitator, and some trouble was encountered in the inrush of air through these holes. To minimise it the small sheds in which the terminals were housed was made, as far as possible, air-tight, but the tubes immediately beneath the holes always worked a little less efficiently than the others. To overcome this difficulty, it is suggested that the insulators should be above the precipitator, and that the electrode bar should enter at the top from an insulator which, while admitting no air, would be removed from the action of heat and fume. This would be secured by the method of mounting proposed.

The burner was at first run with only half its normal charge, *i.e.*, with 6 tons of ore per day. In these circumstances, the

[1] *Chim. et Ind.*, 1920, 4, 291.

highest temperature that could be reached during a run was 300° before the precipitator and 130° after. This was found to be too low, and to lead to the formation of a deposit on the electrodes which contained acid and was very difficult to detach. After increasing the charge from 6 to 10 tons, these temperatures rose to 340° and 260°. The efficiency of the apparatus was greatly increased by this change, and the deposit

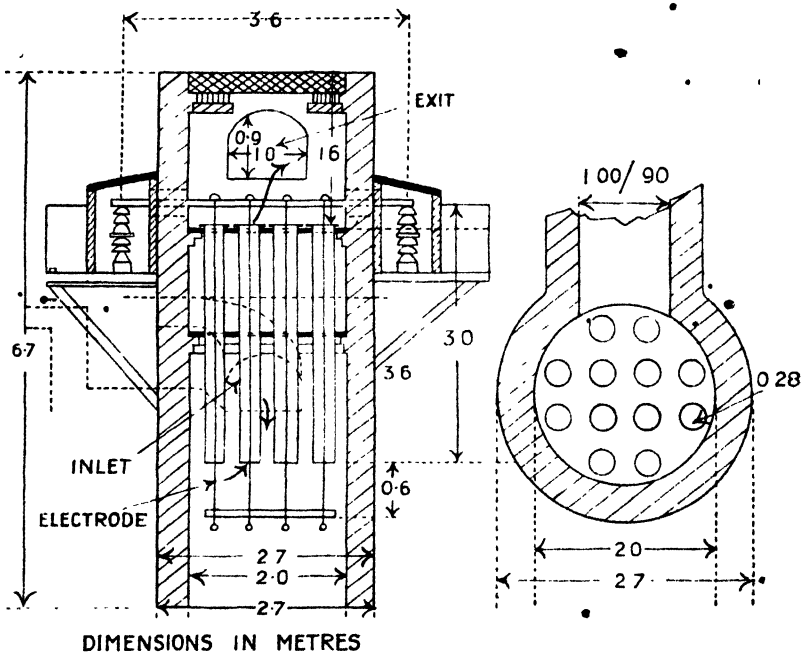


FIG. 47.—Experimental Electrostatic Dust-Separator.

was non-adherent and readily fell to the bottom. From this point of view—ready clearance of any deposit formed—flat electrodes were considered likely to be much superior to tubes. Agglomeration may always be expected below 250°. If it cannot altogether be prevented, some mechanical device for detaching the deposit is advisable. It is stated that the tests were made under conditions which, although inevitable, were unfavourable to comparative testing. The following table gives the results of the several runs. The last column contains the values calculated for the mobility of the particles. This quantity is the velocity (in cm./secs.) due to the action of a

potential gradient of 1 volt per cm. It is shown that, if U is the effective voltage and V the greatest permissible axial velocity of the particles (*i.e.*, the velocity in column 3, below, for those experiments in which precipitation was very nearly complete), the mobility K is given by $K = 1{\cdot}515\ V/U$, for this series. The values of K which may be used, as mean figures, for the purposes of design, are, at 230°, 40×10^{-4}, and at 310°, 57×10^{-4}.

Voltage.	Per cent. SO_3 before.	V. cm./sec.	v. Mean.	Current. $\times 10^{-3}$, amps.	Analyses before		Analyses after.		Per cent. of solid precipitated.	K. $\times 10^{-4}$.
					SO_3 gm/m³.	Insoluble.	SO_3 gm/m³.	Insoluble.		
44700	3·8	130	235	16·0	10·22	3·26	2·88	0·1050	96·5	44·0
35400	4·2	117	240	8·0	9·93	2·63	2·90	0·2800	89·5	...
47700	4·0	116	210	20·0	3·28	2·97	1·50	0·0002	99·5	37·0
42000	4·2	116	235	17·5	3·92	1·41	3·17	0·1000	93·0	...
46700	4·0	126	248	25·0	10·00	2·38	1·79	0·0300	98·7	41·0
53000	4·1	134	286	50·0	9·61	1·90	6·75	0·0098	99·9	38·4
41000	3·5	166	301	25·0	8·75	2·30	8·20	0·0065	99·5	61·5
45500	3·8	161	318	37·0	8·79	1·15	5·35	0·0098	99·9	57·7

Some further information regarding the electrostatic precipitation of acid mist, previously freed from at least most of the accompanying dust, is given in the last section of this chapter. From the two papers already quoted (the first of which gives a number of references) a very useful account of the practical aspect of electrical precipitation in general, can be gathered.[1]

Cooling the Burner-Gas.

According to Knietsch, the removal of mist from the burner-gas is rendered much more difficult if it is cooled quickly. Although long flues are in use—as at Höchst,—where a leaden flue 7 ft. by 5 ft. and 150 yards long takes the product of the Wedge mechanical furnaces, this slow cooling is by no means general or even advisable. As in the rest of the purification plant, the only metal with which condensed acid may come into contact should be lead, and as lead will not stand a high

[1] See also, Bush, *J. Soc. Chem. Ind.* (*Review*), 1918, 389; and Gibbs, *ibid.* (*Trans.*), 1922, 41, 189, who discusses the general problem of dust and fume in industrial gases.

temperature and retain its shape, the cooling is in most cases fairly sudden for at least a fraction of the required fall in temperature.

Gas-Coolers.—Lead pipe-coolers are of various designs. The pipes are more usually set vertically and made of heavy lead, and are sometimes banded on the outside with steel bands covered with thin sheet-lead. This banding tends to prevent the collapse which occurs if overheating takes place due to failure of the water spray. (There is usually a slight suction inside the pipes.) It is necessary entirely to cover the steel banding straps with lead, as electrolytic action would otherwise result in the steel being rapidly eaten away. The pipes vary in diameter from 12 to 20 in. or more, according to the amount of gas to be handled, and are arranged in several ways. It is necessary to provide cleaning doors for each bottom connecting-pipe, in order that the accumulation of acid sludge which always forms may be washed out, and provision must be made for the acid condensed in the pipes to run into catchpots provided with lutes. The amount of acid condensing in the gas-coolers is by no means large, and is insufficient to wash out the sludge which is formed at the same time. Cleaning doors or removable covers are also provided at the head of the vertical pipes, to allow of thorough washing down.

A design which is employed in the United States is shown in the sketch of Fig. 48. The pipes are usually of about 12 in. diameter, and are erected in parallel sets, each set running from a bottom to an upper header of larger diameter. Several such sets are connected by joining the headers in the way shown in the first half of the sketch. The gas usually enters at the top, passes down one set into the lower header, and then up the next set, and so on. The vertical pipes are sprayed with water, and the bottom headers are provided with luted catchpots of large size to permit draining off the condensed acid, and also to allow of opening the end of the header and quickly flushing out the accumulated sludge. The size of the vertical pipes is diminished in each succeeding set, to compensate for the diminution of volume due to cooling, but the number of pipes in each parallel is usually the same. This type of installation is said to be more expensive to erect than one consisting of horizontal pipes, but is much more efficient and less trouble to

operate.[1] The usual method of cooling is to run water down them from perforated water pipes which encircle each lead pipe near the top; but if water is not too plentiful, very good results

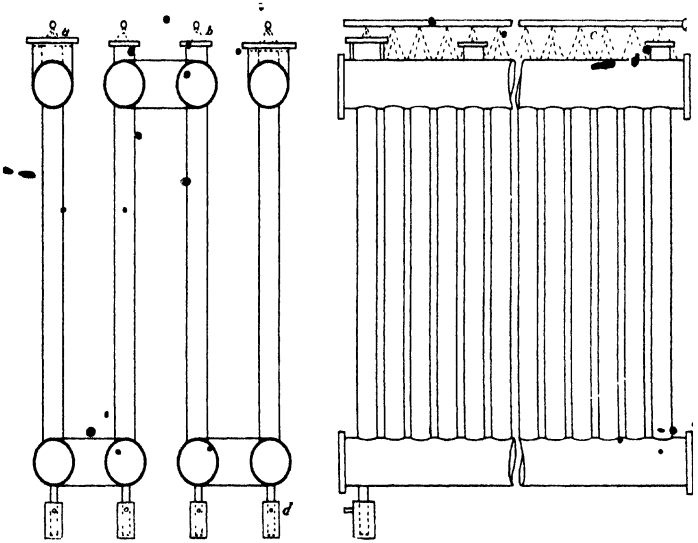


FIG. 48.—Vertical Burner-Gas Cooler.

can be obtained by spraying the water on to several pipes at once from large atomising sprays of the Gaillard type. This effects a great economy in water.

With the installation just described (see also U.S. P. 113437) the rate of travel of the gases is lower than if the pipes had been arranged in series. A good example of the series arrangement, illustrated in Fig. 85, p. 299, is that of the gas-coolers used on the Grillo plants of H.M. Factories. The method of arranging the pipes is shown diagrammatically in Fig. 49. The gas enters at the top of one pipe and leaves at the top of another. The bottom headers, each joining two pipes, all

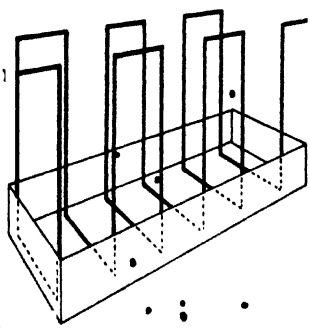


FIG. 49.

[1] *U.S. Dept. of Int., Bull.* 1920, 184, 155.

lay in the same direction and were arranged in a shallow wooden tank which was kept full of water. The diameter of the pipes was in this case 20 in., and two sets of twenty each were worked in parallel. The cooler as a whole could easily deal with 4 to 5 million cub. ft. of gas per day, and it was rarely that water was used on all the pipes at once. The gas entered at about 280° and left about 30°.

In some plants the pipes are built up horizontally and immersed in water. To obtain the cooling surface required with a minimum initial cost, they are often very long and of large diameter. The removal of sludge from long horizontal pipes is a matter of some difficulty. Catchpots are fitted for the condensed acid at frequent intervals. For the sludge, cleaning doors are fitted to the upper surfaces of the pipes, through which flushing-out may be carried on. A horizontal submerged cooler of this kind is illustrated in Fig. 50.[1]

Whichever system of erection be employed, the method of connecting the dust chamber and the cooler is of great importance, for at this point, where temperatures up to 300° may obtain, the corrosive action of the acid, near to the point of liquefaction, is intense. No acid should ever be allowed, of course, to condense in the dust chamber, but the maintenance of the necessary high temperature at the outlet of the chamber places a certain strain on the cooling of the first pipes of the cooler, and if the water supply to these fails their collapse may be very sudden. The best type of connection is probably iron- or lead-covered porcelain pipe of the "Ceratherm" variety. Steel pipes lined with tiles set in acid-proof cement have been used, and the brick flue from the dust chamber has also been carried nearly to the entrances to the lead cooling-pipes, and connected to them by a short and easily renewable length of steel pipe.

Even though the first lead pipes of the coolers are maintained without collapse, the action on them of the hot concentrated acid which condenses is severe, and the General Chemical Company in one of the Herreshof patents of 1910 express the opinion that no merely external cooling is sufficient (U.S. P. 955067 of 1910). They devised, therefore, a stand-pipe cooler, the inside of which is wetted by a descending film

[1] *U.S. Dept. of Int., Bull.*, 1920, 184, 154.

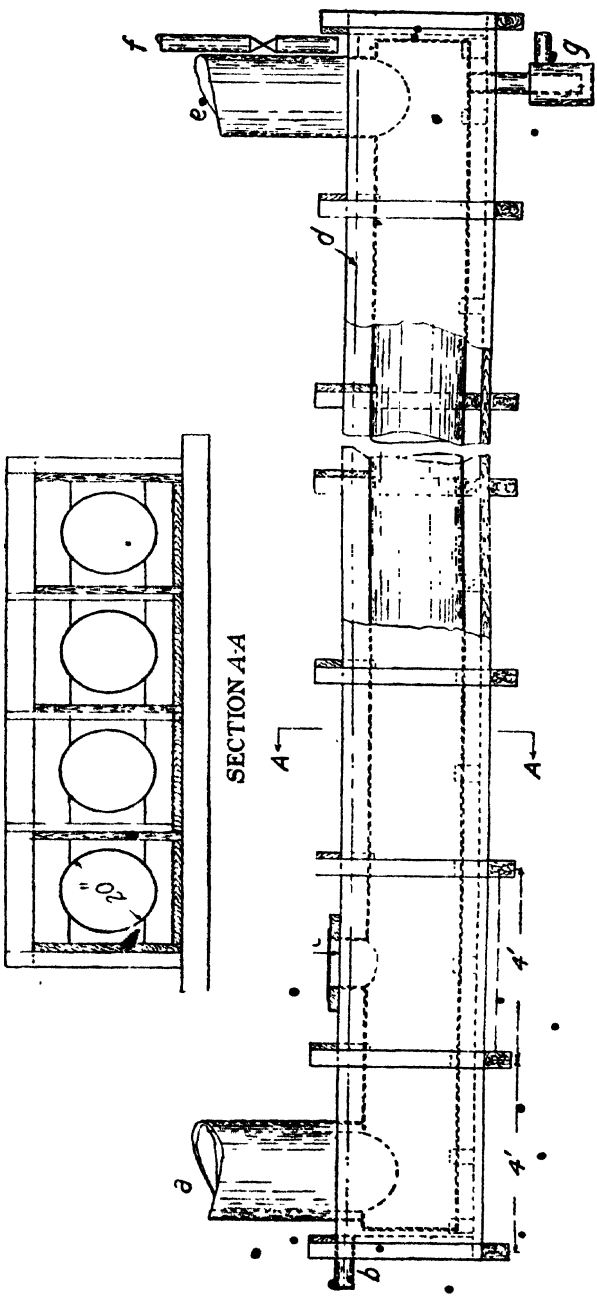


FIG. 50.—Horizontal Submerged Lead Cooler.

a, Gas inlet; *b*, water inlet; *c*, washout; *d*, water level; *e*, gas outlet; *f*, cooling water; *g*, drain.

of diluted sulphuric acid, the outside being water-cooled in the usual way. This is illustrated in the sketch of Fig. 51. The gas enters by the side pipe into the portion of the cooler which is surrounded by water in the jacket *j*. Here, and on passing upwards, it is prevented from attacking the internal walls by a film of acid which is formed by running in acid from the constant level tank *a*, and allowing it to flow through the gas-lute *l*, and down the inside of the cooler. Access to the main header H is controlled by a butterfly-valve *K*, the spindle of which also carries a gas-lute, and the cooling pipe is fitted with a guard *g* so that the acid, instead of running into the off-take and so into the header, is deflected into the annular channel *h*, and, overflowing the rim, again descends the inside of the pipe.

Another variety of gas-cooler is that employed in the Tentelew plant. It consists of a cylindrical vessel built up of a number of cylindrical sections provided with hollow diaphragms. Water is circulated through these diaphragms and surrounds the whole cooler. This is represented in Fig. 105, p. 356. This arrangement facilitates cleaning out. The sludge is more readily removed than from pipe systems, and there is less tendency for the apparatus to be blocked up in use.

Cooling by Contact with Acid or Water.—The hot gas may also be cooled by bringing it directly into contact with diluted sulphuric acid, or even with water. The gas then passes on at a lower temperature, laden with the water vapour which has been evaporated.

This mode of cooling formed part of the system of purifying burner-gas worked out by Rabe which is still operated in a modified form. The hot gas was cooled by direct contact with the liquid, in two stages. In the first the effect was such that the liquid evaporated more or less completely, and in the second stage it was only heated. The gas entered a cooling chamber consisting of a cast-iron pipe lined with acid-proof material, and by means of a Korting's spray producer sulphuric acid or water was injected in such amount as to be entirely evaporated. The cooled gas then passed into a tower built like a Glover tower, the bottom and sides being lined with acid-proof pottery. Contact with the acid flowing

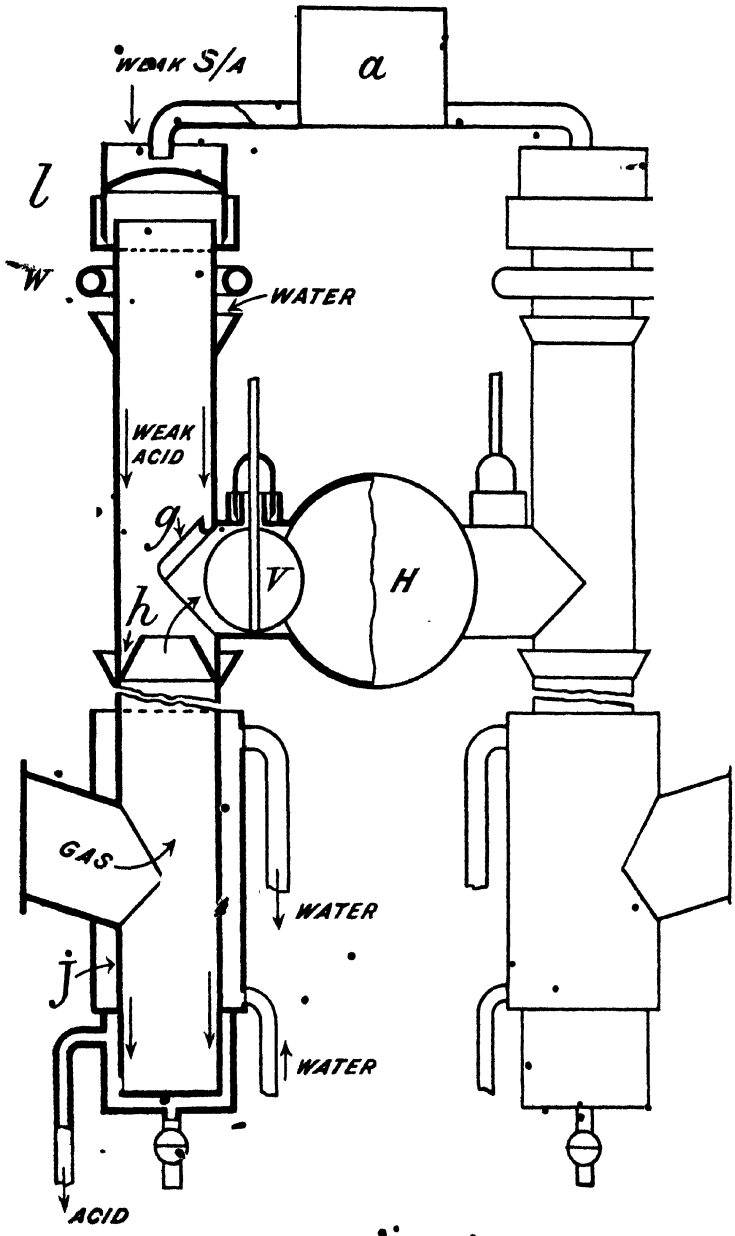


FIG. 51.—Stand-Pipes with Internal Cooling by Acid.

down this tower completed the cooling (B. P. 3327 of 1901). The same principle is embodied in one of the Herreshof patents (U.S. P. 940595 of 1909), which gives a general outline of a purification method. From a dust-chamber the furnace-gas passes to three towers, down which is run weak sulphuric acid from the scrubbers of the purification system.

The heat which is removed is thus utilised for the concentration of weak sulphuric acid; but an extra burden is thrown on the drying system of the plant, unless special means are taken for removing the extra water vapour. In some plants which were erected in this country recently with Glover towers for cooling the gas and concentrating weak acid at the same time, it was found that the arsenic content of the cooling acid rose so rapidly that to keep the arsenic down to a commercially possible figure, a large amount of acid had daily to be removed from that circulated through the tower, the concentration attainable thus being lower than was desired. This difficulty would appear to have been in view in a patent of 1910 (Duron and Hartmann, B. P. 9869 of 1910), in which it is proposed to filter the burner-gas through a layer of ferric sulphate or similar material to remove the coarsest impurities, and then to treat it in a series of chambers with sprayed sulphuric acid.

The elimination of the additional moisture introduced by this procedure is dealt with in a recent Herreshof patent (U S. P. 1113437), based on the observation that the rapid cooling of burner-gas which has been scrubbed with 50 per cent. sulphuric acid caused a considerable separation of condensed water containing very little acid. The process is essentially one for removing water only, and is applied between the cooling scrubbers and the filters, so that stronger acid is obtained by deposition in the latter elements of the plant. It is stated that a suitable cooling range is from 93° to 38°. Hot gas of 7 per cent. dioxide is reduced in temperature to 500° in suitable conduits, is then passed through towers containing 50 to 60 per cent. sulphuric acid, so that its temperature falls to between 90° and 120°, and at this temperature enters large pipe-coolers constructed on the same principle as those illustrated in Fig. 48. Instead of cooling by scrubbing, the injection of a spray of water can be resorted to.

The sulphuric acid is usually less than 4 per cent. of the total condensate.

In many plants in which this acid-cooling system has been fitted,[1] there are two towers. The hot gas enters the first, and after being cooled with comparatively strong acid, enters a second in which weaker acid is circulated. A large amount of acid is removed from the gas, and water driven out of the acid in the first tower is transferred to the second. The strength of the acid in the second tower is thus dependent on the operation of the first, and to reduce it sufficiently water is sometimes added. It is found that the higher in temperature is the gas which enters this system, the greater is the amount of mist which passes away from it.

Gas-filtration.

Filtering Materials.—Of the many substances which have been used as filtering materials, coke and quartz are the most common. Both these materials are unattacked by sulphuric acid of any concentration (below 100 per cent.) at the atmospheric temperature, but if the temperature is expected to be considerably higher than this, coke is not always considered to be sufficiently resistant. Silica has the advantage of being readily washed and dried, and of being recoverable in a clean condition no matter how much it may have been fouled. Coke is more often renewed than recovered, and is in any case very difficult to obtain quite dry. Where the conditions of use are such that only traces of acid are to be extracted, coke undoubtedly exposes the larger surface; but if sufficient acid is thrown down to wet the filtering material there should seem to be very little difference between the two. Hard "metallurgical" coke is employed.

Many other materials have been and, in some cases, are still in use. Asbestos is used in Grillo plants, basic-slag sand in Mannheim plants, as well as asbestos mixed with lime. Filtration through calico held on perforated iron frames has been reported in recent use at Höchst. Cotton-wool filtration was a distinguishing feature of the process used at the *Müldener* works at Freiberg. Slag wool, sawdust, and wood-shavings have all been used. The material made by heating cotton

[1] See for instance, p. 336.

in a closed vessel to 300° or 350° has also been suggested (Fr. P. 456524).[1] In all these instances the main action of the filtering material on the impurities in the gas is the purely physical one of causing adherence of particles of mist or dust. It is widely believed that basic-slag sand has a chemical action on arsenical impurities, but the foundation of this does not seem to be very certain. Hydrochloric acid is retained by slag sand, and slag wool is said to have to some extent the same effect.

The size, construction, and filling of filters varies greatly. No general figures for the efficiency of quartz or coke filtrations can readily be given, because there are so many factors which vary from one design to another, and the work which is expected of the filters may also vary greatly. A rough division may be made between filtration to remove the coarser particles of acid mist from the burner-gas as soon as it leaves the coolers and before it is scrubbed or washed, and filtration as a final process of purification, applied after scrubbing and perhaps after drying also. The Grillo plants of H.M. Factories had two filters connected in series between the gas-coolers and the scrubbers, each being 30 ft. long, 12 ft. wide, and 10 ft. deep, and usually containing, in addition to coarse material, 4 ft. of crushed coke sized from $\frac{1}{8}$ in. to $\frac{3}{16}$ in. The burner-conversion averaged about 2·5 per cent., so that when 22·5 tons of trioxide were being made per day about 0·56 ton of trioxide had to be removed in purification. Of this the two filters mentioned were responsible for 60 to 70 per cent., so that if the coarser filling of the filters be omitted from consideration, 1 cub. ft. of coke separated about 0·44 lb. of trioxide in the form of 50 to 70 per cent. sulphuric acid. For every ton of trioxide made there were about 130 cub. ft. of fine coke.

Several variations in the method of passing the gas through the filtering material are possible. It is general to support the coke or quartz on a grid of lead or acid-proof bricks, and to pass the gas through from the bottom. But if the filter is the first in series after the burners, and deposition of dust is expected, or sublimation of sulphur from sulphur burners, the gas is often passed in at the top, so that the contaminated material can, if necessary, be replaced. Flushing pipes are sometimes fitted at either top or bottom by which the accumulated

[1] *Metallbank und Metallurgische Gesellschaft*, Frankfort.

impurities are washed out. A good instance of coke filters in which the coke is supported on a brick grid is seen in the Grillo filters already mentioned, the constructional details of which are shown in Fig. 86. In the first two of these, the gas passed downwards; in the other three, which were placed after the scrubbers, it passed upwards. The body of such a filter consisting of nothing but a lead box, it was found necessary to provide very rigid supporting woodwork, and to band the lead sides and top to the wood very thoroughly in order to avoid the crystallising effect of the pulsations set up by the blower. This was especially necessary in the last filter, from which the gas passed immediately to the blower.

Another type of filter which has been used extensively in the United States is that illustrated in Fig. 52. It consists of a large rectangular lead lined wooden box which is entirely filled with carefully sized and washed coke. For a plant producing 24 tons of trioxide per day, this box would contain from 180,000 to 360,000 cub. ft. of coke, in order to remove only the mist remaining after the scrubbing operations. The bottom slopes slightly towards the centre, and a shallow drain runs longitudinally down the middle of the bottom and discharges into a trap at one end. The gas entrance is usually placed at one end near the bottom; the outlet is at the other end, usually near the top, and round both entrance and outlet is provided a large gas-diffusing space, in such a way that the largest possible area of the coke is accessible without risk of the entrances to it becoming blocked. Coke from $\frac{1}{4}$ in. to $\frac{3}{8}$ in. is used. Lead strips or lead-covered ribs are fastened to the under side of the cover, so that they extend across the filter and project well down into the coke, thus preventing the gases from passing through an empty space at the top, in case the subsidence of the coke causes one to form.[1]

It is, of course, necessary in this case that the entering gas should have been scrubbed quite free from all fumes of solid matter, for no upper layer of coke can here be replaced. It is, however, possible to wash out deposited solid matter from the top; but such operations are not successful owing to the difficulty of distributing the washing liquid over the coke, and the great probability of channels being formed as it runs down.

[1] *U.S. Dept. of Int., Bull.*, 1910, 184, 160.

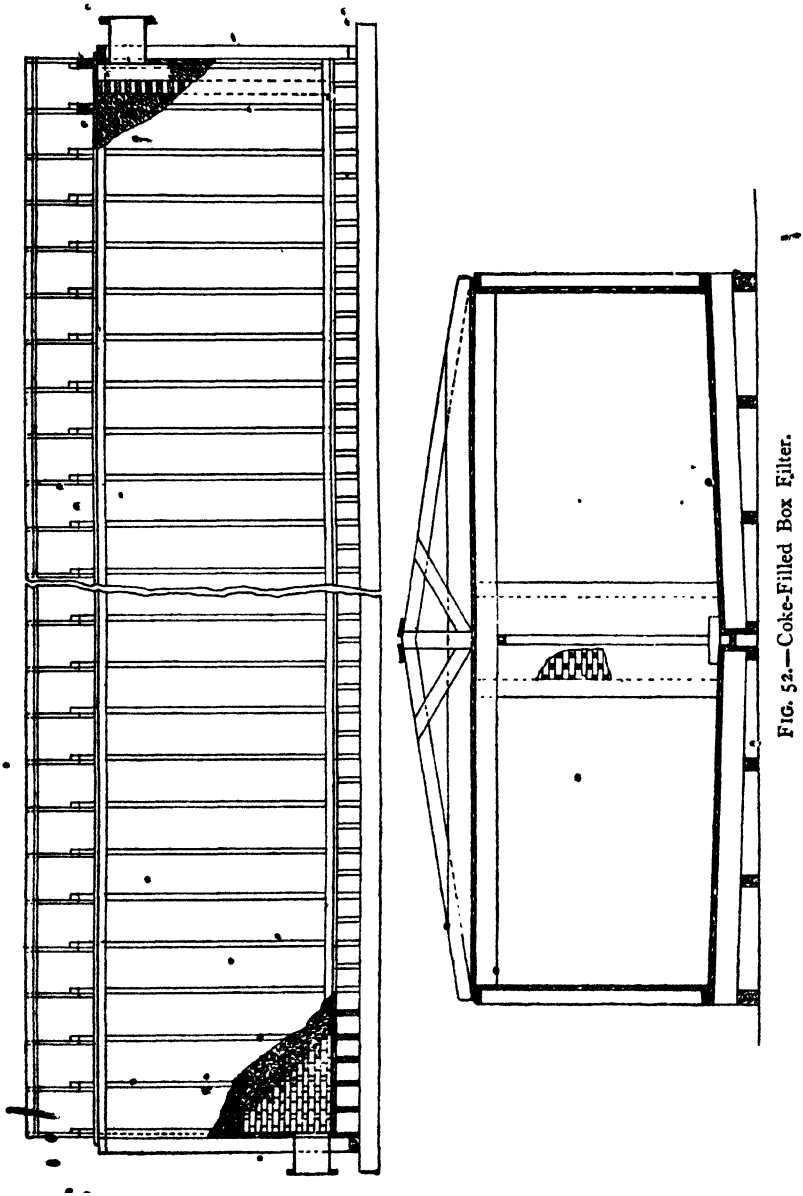


FIG. 52.—Coke-Filled Box Filter.

Another system of gas-filtration consists in arranging a number of smaller filters in sets of three or more in series, as

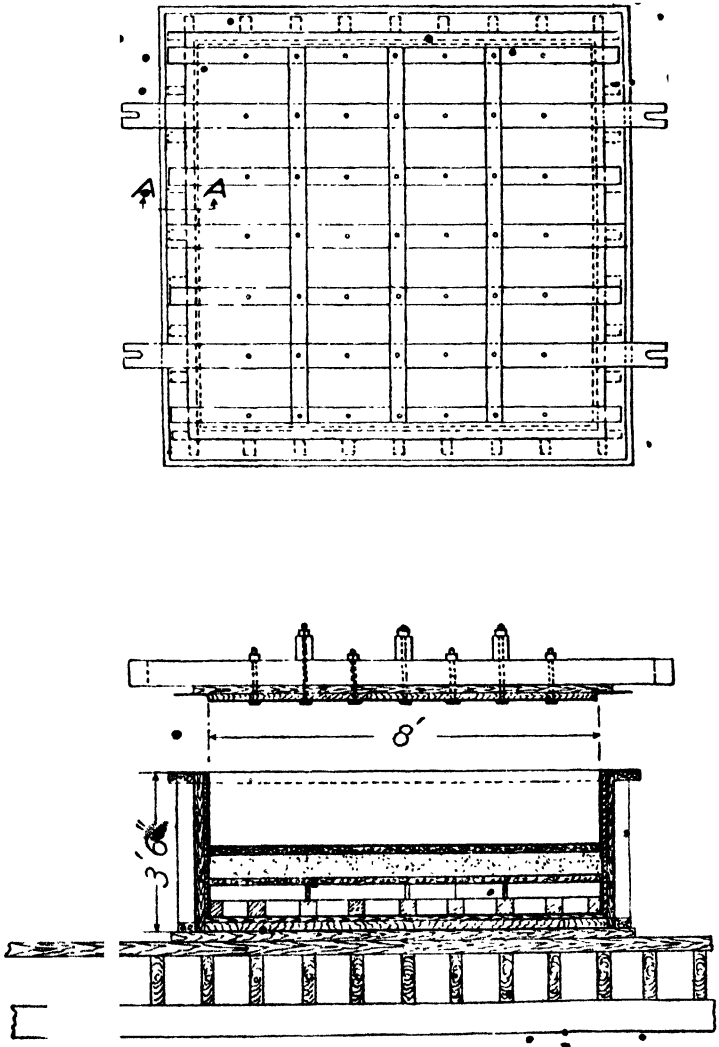


FIG. 53.—Small Box Filter for Asbestos or Sawdust Packing.

many sets being connected in parallel as may be required, suitable provision being made for switching over to spare filters for cleaning. Such installations are in use in the United

States for the final stages of purification, and often consist of a number of boxes (Fig. 53) 8 or 10 ft. square and 2 to 3 ft. deep, of substantial construction and lead-lined both inside and out. The filling consists of light material, such as sawdust or asbestos, which offers little support to the sides, and collapse is prevented by the outside covering which resists the suction. The top is in one piece, lead lined and heavily ribbed on the outside. Heavy timbers project in four directions and can be used for raising the top with jacks. The lead lining of the top projects half way across the strip made by flaring out the inner lining of the filter, and a joint can be made easily by beating down the top lining and luting it with suitable plastic cement. The gas inlet is in the centre of one side at the top. Good results are obtained only when the gas passes *down* through the filter, and the gas outlet is therefore on the opposite side near the bottom. Each box contains a brick or tile grill about 1 ft. high. On this straw is spread, and on this again about 6 in. of coarse pine sawdust covered with coarse canvas. The second box of a set has, in addition, a layer of finely teased, long-fibre asbestos, covered with canvas. In the third box the asbestos and some of the sawdust is replaced by mineral wool to trap any hydrochloric acid which may have passed the scrubbers. In normal operation there is a considerable drain from the first filter, and occasionally a little from the second, but there should never be any from the third. When a filter is becoming clogged, as shown by a differential pressure gauge fitted to each one, the whole set is switched out of the circuit and a clean one switched in. It is usual to renew the first filter every seven days, the second every three or four weeks, and the third every six or eight months. Such a set is said to be capable of filtering 5 cub. ft. of gas per minute for each square foot of total filtering area, without causing undue resistance to the flow.[1]

Another instance of the arrangements of filters in parallel is that adopted on the Tentelew and other plants, not for final purification, as in the last case, but for the initial stages. The filters are usually cylindrical and are fitted with luted bends to the gas entrances and exits, so that any filter can be cut out for cleaning. Water and compressed air-pipes are fitted so that by filling the filter from the bottom, and possibly also with the

[1] *U.S. Dept. of Int. Bull.*, 184, 162.

assistance of compressed air, the deposited impurities may be dislodged from the silica and run to waste. Further details will be seen in the sketch of Fig. 107, and in the general description of the Tentelew plant.

Scrubbing.

The scrubbing of the burner-gas may be carried out by a variety of methods which are divisible broadly into two classes. In one the gas is passed through a tower down which the scrubbing liquid descends, well distributed over suitable packing. In the other the gas is brought into intimate contact with the liquid by being bubbled through it. The second class of operation is much the more efficient. Mechanical scrubbing with such plant as the Theisen centrifugal scrubber used for cleaning blast-furnace gas from dust, or the Trepex washer, has often been discussed. An American patent (Webster and Perry, U.S. P. 1390410 of 1921) embodies a claim for the application of a centrifugal gas-scrubber, revolving at 20,000-40,000 r.p.m. Sulphuric acid is fed in as absorbing liquid and is brought into violent impact with the mist by the centrifugal action. The possibilities of this kind are promising, but so far, no doubt mainly on account of practical difficulties, they do not seem to have been realised.

So far as the removal of fine dust is concerned, there is perhaps no special difficulty in the Contact Process as compared with other known processes; but sulphuric acid mist constitutes a special and difficult case, for the particles are unusually difficult to settle, even in presence of a large amount of water vapour which might be expected to dilute them rapidly to the point of deposition.

The scrubbing liquids in use are water, dilute sulphuric acid, and very dilute alkaline solutions. If water is used, the amount is naturally limited, since too much sulphur dioxide would otherwise be removed and lost, so that in the later stages of the washing operation, the water has been converted into dilute acid. Dilute acid alone, if the scrubbing is very thorough, is efficient in removing most of the impurities but, as has already been seen, is not very efficient in dealing with considerable quantities of hydrochloric acid. A dilute solution of sodium hydroxide, as used in the Tentelew process, is

satisfactory in this respect and is one of the most perfect means of purification. The actual reagent is of course a small amount of bisulphite, dissolved in a large quantity of water.

Scrubbing in Packed Towers.—In the purification method usually adopted in Grillo plants, the burner-gas, possibly after some preliminary filtration, is passed through two or three towers in counter-current to descending streams of acid. Concentrated sulphuric acid is used in the last of these towers in order to dry the gas, so that the set performs the double functions of scrubbing and drying. The towers are usually packed with coke, and arrangements are made, at least in the case of the last one or two towers, for cooling the acid as it runs off, before it is again passed to the top. If three towers are used, the heat developed in the first (containing the most dilute acid) is not enough to make such an arrangement necessary. Details of the construction and lay-out of such a set will be found in Figs. 87 (1) to (3). Each tower, with its top and bottom acid tanks, distributing plate and pump, forms a separate system for circulating acid, and the concentration of the acid in the three towers is controlled by forwarding acid from one bottom tank to another as required. It was usual to maintain the acid in the last tower at 93 to 95 per cent., that in the second at 84 to 85 per cent., and that in the third at 55 to 60 per cent., water being added in the last case if necessary. Large feeds of acid up to 10 tons per hour were thrown into each tower.

The efficiency of such a scrubbing system in regard to chlorine has already been discussed. It is entirely dependent on working the first scrubber with as weak acid as possible, and renewing it frequently. As regards purification from acid mist and its accompanying impurities, such means are in themselves quite insufficient without very thorough subsequent filtration. Some filtration is in any case necessary to prevent finely divided acid being carried forward, and if the feeds down the towers are very heavy, the mist trouble may be made worse rather than better. The total amount of acid and water vapour passing from these towers varied greatly, but amounts of 0·5 gm. per cubic metre of H_2SO_4 were often found, accompanied by 0·2 gm. or more of water. On maximum production of the plant the "total moisture"

was in some cases 1·0 gm. or more. The extent of packed scrubbing space was 346 cub. ft. per ton of trioxide made.

In the scrubbing system which has been outlined, the amount of concentrated acid which has to be added to the last tower in order to maintain the acid concentration at a figure consistent with complete drying, say at 95 per cent., will depend on the amount of water vapour which passes over from the first tower, and this quantity again will be the smaller, the lower the temperature of the acid in the first tower. If the entering gas is hot, or contains large amounts of water vapour from previous treatment with water or sulphuric acid at a higher temperature, the temperature in the first tower will tend to rise. To counteract this and cause the moisture to deposit in the weaker acid instead of the strong, a system of scrubbing with acid flowing over leaden cooler-coils has been designed.[1] One design on this system is shown in the sketch of Fig. 54. In the annular space between the inner and outer lead shells, spirals of lead pipe are arranged, with very little clearance—not more than $\frac{1}{4}$ in. to $\frac{3}{8}$ in.—and each spiral is staggered in relation to the adjacent ones. From fifteen to thirty of these spirals are placed one over the other, and one end of each is burnt into the wall of the inner shell which serves as a water reservoir. The other ends of the spirals are brought through the outer shell and provided with valves for regulating the water supply to the coils. Weak acid enters the top of the tower and is showered down on to the coils from a distributing pan. The gases pass upwards between the coils. By these means the heat of the gases is transferred to the acid, which is almost continuously in satisfactory thermal contact with the lead surface. From 11 to 45 C.H.U. are said to pass per hour per square foot of lead, depending on the gas-speed and fineness of division of the acid.

The acid is discharged through the trap into one of two lead-lined settling tanks. The solid impurities settle out, and practically clear acid overflows and is returned to the tower through a pump or air-lift. If this tank becomes too foul or saturated with chlorine, it is cut out and replaced by the other.

[1] *U.S. Dept. of Int., Bull.* 1920, 184, 157.

Scrubbing in Gas-Washers.—The gas-washers used at the

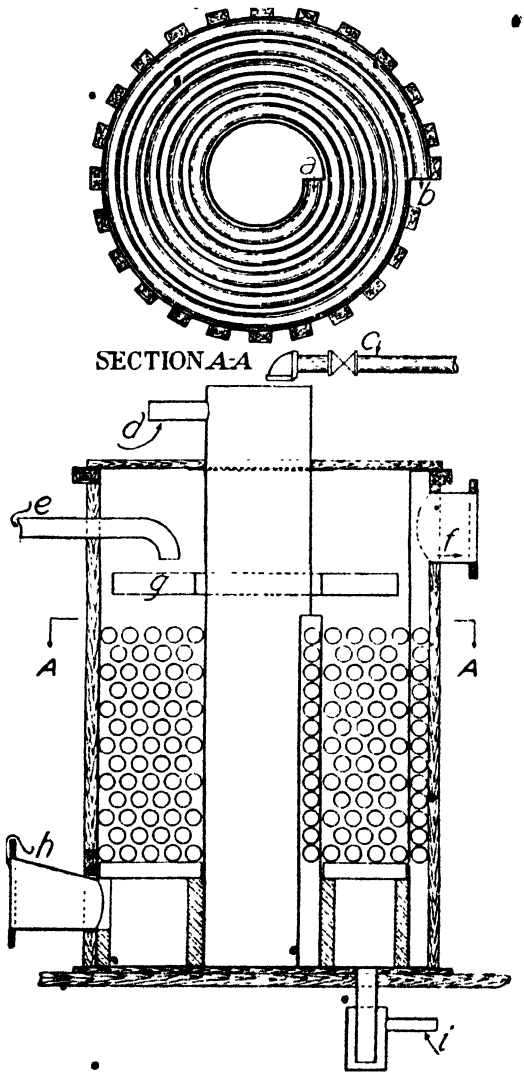


FIG. 54.—Lead-Coil Cooling and Scrubbing System.

a, Water inlet; *b*, water outlet; *c*, cooling water; *d*, water-overflow; *e*, acid inlet; *f*, gas outlet; *g*, pan; *h*, gas inlet; *i*, acid outlet.

Badische works, where the process of purification by intensive washing with sulphuric acid was first developed, are shown in

Fig. 55. They consist of leaden sheets containing a conical leaden bell perforated with holes. The gas passes downwards into the bell, and upwards through the holes, being divided into small bubbles which rise through the washing liquid. The whole vessel is water-cooled. After issuing from these washers the gas is conducted through a series of four rectangular lead-lined washers constructed in the same way, and of the same dimensions (4 ft. by 7 ft.). As before, additional purification is necessary, and the next stage is passage through leaden towers 15 ft. high by 8 ft. diameter packed with coke to remove acid mist. Only drying then remains to be done.

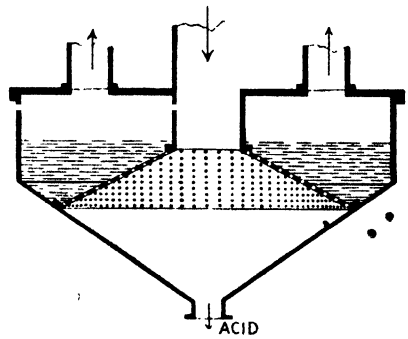


FIG. 55.—Badische Gas-Washer.

Washers of this or a similar type are very efficient as compared with packed towers, and lend themselves more readily to control of the temperature of the acid; but they are at a disadvantage in respect of the power required for operation. A properly packed scrubbing tower in full operation shows a difference in pressure of a few tenths of an inch of water at most, whereas the pressure fall in the case of a gas-washer cannot be less than the head of liquid above the holes. Further details of the action of apparatus very similar to this will be found in connection with the Tentelew plant. See, for instance, the sketch of the "prewasher" in Fig. 108, p. 360.

Washing with dilute soda solution is a distinguishing feature of the Tentelew process of purification, and is carried out in leaden towers built in sections, each section constituting a liquid seal through which the gas must bubble on its upward course. Communicating pipes allow of the overflow of liquid from one section to another, and of each section being completely emptied when necessary. This is illustrated in the diagram of Fig. 109, representing two sections of such a tower.

This scrubbing with water in gas-washers is one of the most efficient methods for removing acid mist, arsenic, and hydrochloric acid. It is easy to see that the intimate contact must

cause the mist globules to absorb water until their concentration falls nearly to that of the washing liquid, so that they become far more readily precipitable, even if the washing liquid does not absorb them bodily. The soda is an additional advantage; lime has been tried but does not give equally good results. A plant producing about 10 tons of trioxide requires only about a kilogram of sodium hydroxide a day, for the liquid in the top section of the tower is rapidly converted to sodium bisulphite, and as this descends through the other sections, it is gradually converted into sulphuric acid of greater or less concentration, so that the washing is really carried out by two separate reagents, anything which escapes the sulphuric acid being retained by the bisulphite.

It is a very notable fact that in at least one modern plant—that at Dormagen—the cooling and washing of the burner-gas is carried out in a single tower. The burner-gas from the four 5-ton Herreshof furnaces of each unit passes first of all through Cottrell dust-precipitators of the general construction indicated in Fig. 46. From this it is led to a large tower composed (externally) of five cast-iron sections bolted together, the whole being about 30 ft. high. Each section of the tower communicates with those above and below it by small pipes. Water is admitted at the top, and a drain is provided at the bottom into a lead lined launder. The gas leaves this apparatus at about 35° and, after drying, is passed to the converters without further treatment. Fig. 56 shows this in rough diagrammatic form. The internal construction of this tower has not been revealed, but since the burner-gas entering it must be from 500° to 600° in temperature and issues from it purified, at nearly the temperature of the atmosphere, the installation embodies a very remarkable achievement.

Drying.

The drying of the purified gases is always carried out by passing them through packed towers down which sulphuric acid is allowed to flow. Coke is very generally used as packing material. At least two towers are generally used, and often three. In such towers, especially when they have to fill the double purpose of scrubbers and driers, as described in the last section, the acid is maintained in circulation round each

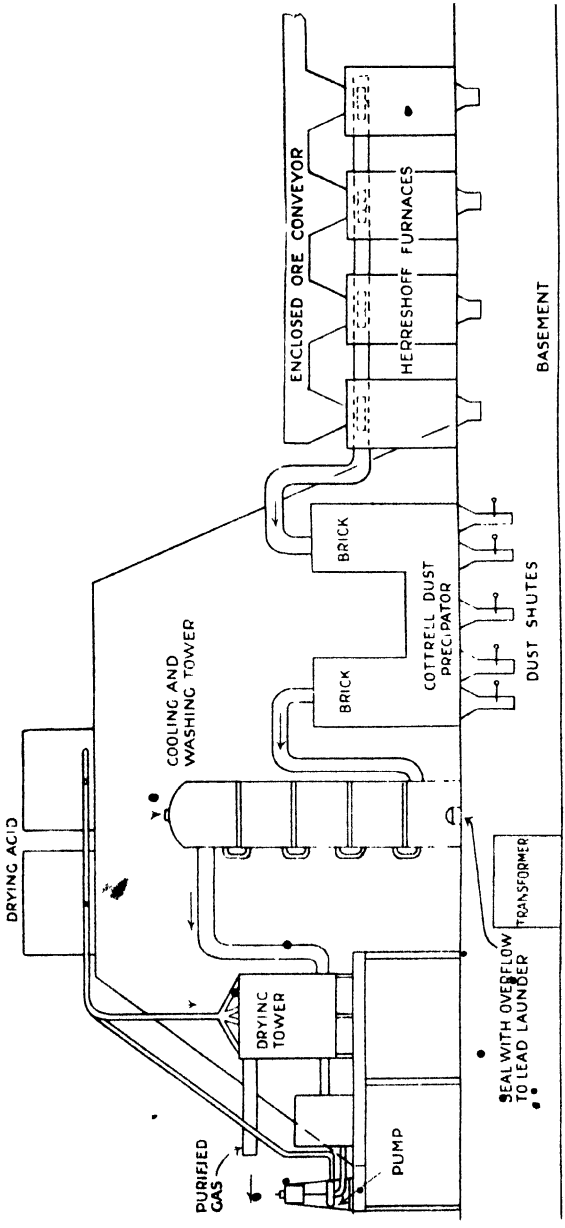

ENCLOSED ORE CONVEYOR
HERRESHOFF FURNACES
BASEMENT
BRICK
BRICK
COTTRELL DUST PRECIPATOR
DUST SHUTES
COOLING AND WASHING TOWER
DRYING ACID
DRYING TOWER
TRANSFORMER
SEAL WITH OVERFLOW TO LEAD LAUNDER
PUMP
PURIFIED GAS

FIG. 56.

tower separately, and sufficient fresh acid is supplied to the tower which the gas enters last to maintain its strength at the figure desired, say 93 per cent., the volume of acid being kept more or less constant by by-passing some to the second tower and some from this to the first.

As will be indicated more clearly in connection with absorption, the amount of water removed from the gas in this way may be an important factor in the operation of the plant. One ton of water combines with 4·44 tons of trioxide to form sulphuric acid, and with 5·80 tons to form oleum of 20 per cent. strength. If there is no outlet for the weak acid from the drying towers, otherwise than to use it as feed acid for the absorption system, the quantity of contained water may be more than is allowable. This condition of affairs will be more liable to arise when recovered acid of 92 per cent. or over has to be concentrated by passage through the absorption system, than when the object is merely to produce oleum from a feed of water, or of weaker acid from the purifying system.

The quantity of drying acid required depends on the initial and the allowable final strength. Suppose that acid of p_1 per cent. H_2SO_4 is diluted in use to p_2 per cent., the weight required to abstract 1 ton of water is then:—

$$a = \frac{p_2}{p_1 - p_2}.$$

If the weight of water vapour in the gas is known—w grams per cubic metre, the corresponding weight in pounds per 1000 cub. ft. is $w/16{\cdot}02$. For practical purposes 1,000,000 cub. ft. is a more convenient quantity. The weight of water in this volume is $0{\cdot}02787\ w$ tons, and the weight of acid required for its absorption is:—

$$A = 0{\cdot}02787\ w \frac{p_2}{p_1 - p_2} \text{ tons.}$$

Such calculations as this can easily be carried out with fair approximation by means of the chart[1] of Fig. 57. A thread

[1] *Construction of the Chart.*—The scale of p_1 is uniform, that of a is reciprocal (graduated partly by calculation, partly by projection of uniform scales from suitable radiant points). The supports are graduated by methods similar to that mentioned in the note on p. 192. The position of the A support is obvious, that of the p_2 line is found by calculation of pairs of values of a and p_1, each having a common p_2.

held tightly across any two points on the scales of p_1 and p_2 gives the corresponding value of a, *i.e.* tons acid per ton water, on the scale of a. Keeping the thread fixed on the left hand (a) scale, move the right hand to stretch the thread over the point required on the w scale; A is then at once read off on the long sloping support. To obtain the whole requirement of drying acid per day, multiplication of the result by the number of million cub. ft. passing through is necessary. This is generally known, and in any case can be calculated very quickly on the basis that 1 ton of sulphur, as sulphur dioxide, occupies (at N.T.P.) 24,500 cub. ft. If the gas has been washed with water or dilute soda, it will be saturated with moisture at the temperature at which it enters the drying towers. To the w scale of the chart is therefore attached a scale of temperature which, for rough approximations, may be used instead of the ascertained water content of the gas.

Only in the Mannheim plant is the air dried before admission to the furnaces. In this case the chart can be used in conjunction with the indications of the wet and dry bulb hygrometer and appropriate tables.

It is not possible to state the degree to which the drying of gas over sulphuric acid, say of 94 per cent., can be carried at a given temperature in the ideal case, because the very small vapour tension of water over acid of this strength has not been determined, but in practice well-dried gas does not contain more than 0·02 to 0·07 gm. of water per cubic metre. Tests made in the laboratory with phosphorus pentoxide as additional absorbent show that the lower figure given is, under ordinary conditions of flow, near to the lowest that can be reached.

The purity of the drying acid is of the greatest importance. The flow of the acid and the inevitable splashing cause small particles to be drawn along in the gas stream, and unless precautions are taken these may find their way to the converters, possibly carrying arsenic with them. The acid should therefore be tested periodically for arsenic. After leaving the drying towers the gas almost always passes through filters in which the spray produced in the towers is removed by passage through fine coke. The size of these filters varies with the design of the plant, and is naturally greater where

the gas has not been thoroughly washed with water, as in the Grillo plant, and some of the original mist (which scrubbing with any strength of acid seems only incompletely to remove) still remains in it. For well-washed gas a moderate amount of packed space is considered sufficient, say about 10 cub. ft. per ton of SO_3, as on plants of the Tentelew type; but in spite of the presence of such filters the purity of the acid must be very carefully watched.

If a contact plant is producing oleum or acid of about 98 per cent. from a "water feed," so long as no arsenic passes to the converters, the product of the plant is free from this impurity, and the drying acid can be made either by direct production of 98 per cent. acid in the absorption system or by "breaking-down" (*i.e.*, diluting) the oleum. But the feed acid which is often supplied to the plant from other sections of the works on which the plant is situated is not always of the required purity, and it is therefore usual to instal a small auxiliary absorption system to make pure acid, or in cases where the number of units is large, to keep one unit working with water alone, and to ensure that no contaminated acid can be mixed with its production. Examples of the installation of such auxiliary absorbers will be found in connection with the various plants described.

It should be borne in mind that the solubility of sulphur dioxide in sulphuric acid is considerable, particularly when the acid contains less or much more than 84 per cent. H_2SO_4. (Figures are given with the data at the end of this chapter.) The acid in the upper and lower tanks of the driers and scrubbers should therefore be protected as completely as possible from the air, so as to maintain as high a partial pressure of sulphur dioxide as possible above the acid. In one case, where the tanks were originally uncovered, 1½ per cent. of the total production was lost in this way from three scrubbers. On covering the tanks this loss was reduced to 0·4 per cent.

Special Means of Purification

Electrical Precipitation of Mist.—The increasing employment of high-tension electricity for the removal of dust has been outlined in a previous section. In such cases the

temperature is maintained above the point of mist deposition, partly to make certain that the deposit is a dry one and is readily removed. The almost complete elimination of solid particles is believed to simplify the subsequent purification very greatly; and this may well be, because the number of nuclei for condensation having been so much reduced, the mist, when it is thrown down, may form in larger globules which are correspondingly easier to absorb.

It is questionable whether electrical precipitation of both acid mist and dust together has much hope of success, for the deposit would be an adherent sludge, the removal of which would be difficult; but in cases where the greater part of the dust has been removed by other means, electrical precipitation has been applied with success. This system is now in operation on the Dalton plant of the British Dyestuffs Corporation. The Research Corporation of New York who work the American patents, report that they have constructed two installations which have been in operation for mist-removal for over a year and a half.[1] The first installation is located in a very dry climate, and weak sulphuric acid is used as a cooling and scrubbing agent between the sulphur burners and the Cottrell apparatus. The precipitator consists of twelve lead pipes 8 in. diameter by 15 ft. long enclosed in a gas-tight cylindrical lead shell. About 750 cub. ft. of gas (measured under standard conditions) are treated per minute, and the temperature of treatment varies from 10° to 66° C. The average of the results of a long series of tests showed that with a sulphur dioxide percentage of 8·1, the percentage removal of SO_3 was 99·56, the power consumption being 2·7 kw. The average amount of sulphur burnt was 3·8 tons per twenty-four hours, with a maximum possible consumption of 5·0 tons.

The second installation is situated in a damper climate where the sulphuric acid scrubber, placed before the precipitators, acts as a drier and operates with 98 per cent. acid. There are two precipitators each containing sixteen pipes 8 in. diameter and 15 ft. long, set in a cylindrical shell, the whole apparatus being made of steel. These two units treat an average total volume of 2600 cub. ft. per minute (measured

[1] Particulars kindly communicated by the Research Corporation.

under standard conditions) in the same range of temperature as before. A long series of tests gave the following average figures. Sulphur dioxide percentage, 8·7; sulphur burnt in twenty-four hours, 13 tons; efficiency of precipitation of SO_3, 99·71 per cent. The average power consumption was 3·2 kw. In plants of this kind the tubes constitute the positive electrodes, and the negative electrodes are wires or rods passing axially through them.

Other Methods.—From time to time methods have been proposed which involve very considerable modification of the usual purification process. A patent taken out in 1909 by Messel (B. P. 22672 of 1909; *cf.* also Fr. P. 414387) states that the greater part of the sulphuric acid originating in the burners can be got rid of by passing the burner-gas through hot coke. The temperature of the coke must exceed 300° and is preferably about 425°. In this way, although the whole of the mist is not at once removed, the elimination of the remainder is very much simplified. In another specification, by the Simon-Carvés Company (Potts and Simon-Carvés U.S. P. 1335257 of 1920), it is proposed to obviate the usual purification by dissolving the sulphur dioxide from the burner-gas in water or another solvent, and subsequently regenerating it by passage of a current of air. This is a reversion to the old procedure of Squire (see p. 13), with the exception that no pressure is required to complete the solution. It is stated that the burner-gas is first passed through a dust chamber and then washed with relatively strong acid, which may at the same time be concentrated. The gas then passes to two towers down which water is allowed to flow in counter-current, the effluent from the second tower (*i.e.*, that further from the burners) being delivered to the top of the first. The sulphurous acid solution after leaving these towers flows first to a preheater which is warmed by the hot burner-gas, and is then pumped over two towers similar to the first pair. Through these towers a current of air is drawn by means of a fan; the solution is fed to the top of the tower nearer to the fan, flows from the bottom and is pumped to the top of the tower into which the fresh air is entering, so that the spent solution meets the air in counter-current throughout. The same mass of water is constantly pumped round this system, and the rate of evolu-

tion of dioxide should therefore equal the rate of absorption. The gas is passed, as a final stage, through a small scrubber and a drying tower. The proposal is an interesting one.

A drastic modification of the purification process, amounting in fact to dispensing with it entirely, is that specified in one of the recent patents of the General Chemical Company (Merriam, U.S. P. 1384566 of 1921). The very great purity of Louisianian sulphur is the basis of the proposal. Sulphur of this kind is burnt in previously dried air and the burner-gas is carried directly to the converters, being cooled on the way only so much that its temperature at the converter inlet is 400° C. or more. The specification indicates two converters, each followed by a cooler. It is pointed out that the sulphur contains arsenic, although in very minute amount, and that if the contact-mass retained the whole of this, there should be no difficulty in detecting its presence in the mass. None can be found there, and the reason that this poison does not function is not easy to see. During the whole process of burning and conversion a temperature of at least 400° is maintained. There is therefore no formation of acid mist; no external heating is required, and the plant is very considerably simplified.

Data relating to Gas-Purification.

Weight of Water in 1 Cubic Metre of Saturated Air* (w).

t° C.	Grams Water.	t° C.	Grams Water.	t° C.	Grams Water.	t° C.	Grams Water.	t° C.	Grams Water.
− 10	2·363	0	4·835	+ 10	9·330	+ 20	17·118	+ 30	30·039
− 9	2·546	+ 1	5·176	+ 11	9·935	+ 21	18·143	+ 31	31·704
− 8	2·741	+ 2	5·538	+ 12	10·574	+ 22	19·222	+ 32	33·449
− 7	2·949	+ 3	5·922	+ 13	11·249	+ 23	20·355	+ 33	35·275
− 6	3·171	+ 4	6·330	+ 14	11·961	+ 24	21·546	+ 34	37·187
− 5	3·407	+ 5	6·761	+ 15	12·712	+ 25	22·796	+ 35	39·187
− 4	3·659	+ 6	7·219	+ 16	13·505	+ 26	24·109	+ 36	41·279
− 3	3·926	+ 7	7·703	+ 17	14·339	+ 27	25·487	+ 37	43·465
− 2	4·211	+ 8	8·215	+ 18	15·218	+ 28	26·933	+ 38	45·751
− 1	4·513	+ 9	8·757	+ 19	16·144	+ 29	28·450	+ 39	48·138

* Smithsonian Tables.

Multiply these figures by 0·06242 to obtain *lb. per* 1000 *cubic feet.*
„ „ „ „ 0·02787 to obtain *tons per* 1,000,000 *cubic feet.*

N.B.—*Grams per cubic metre* are equal numerically to *ounces* (*av.*) *per* 1000 *cubic feet*, within one part in 800.

Data relating to Gas-Purification—continued.

Vapour Tension of Sulphuric Acid (in mm. of mercury).* (10° to 75°.)

Per cent.	10°.	15°.	20°.	25.	30°.	35°.	40°.	45°.	50°.	55°.	60°.	65°.	70°.	75°.
44	4·4	6·1	8·5	11·5	15·5	20·9	28·1	37·4	48·3	...	...	...	...	...
46	4·0	5·5	7·7	10·5	14·5	19·7	26·3	33·6	44·2	59·6	76·5	96·4	...	...
48	3·7	5·0	7·1	9·6	13·4	18·1	23·9	30·5	40·1	53·5	69·0	86·8	107·2	132·1
50	3·3	4·5	6·5	8·8	12·0	16·4	21·4	27·4	35·9	47·4	61·3	77·0	95·6	118·1
52	3·0	4·0	5·8	7·9	10·9	14·5	18·9	24·1	31·5	41·5	54·0	67·9	84·5	104·5
54	2·6	3·6	5·0	7·0	9·5	12·5	16·5	21·1	27·8	36·2	47·2	59·9	74·8	92·6
56	2·2	3·1	4·3	6·0	8·1	11·0	14·2	18·5	24·1	31·0	41·6	51·6	65·0	80·6
58	1·9	2·6	3·6	5·1	7·2	9·1	12·0	15·8	20·4	26·1	34·5	44·0	55·4	68·4
60	1·6	2·1	3·0	4·3	6·1	7·5	10·0	13·0	16·9	21·6	28·7	36·7	46·1	56·7
62	1·4	1·8	2·6	3·6	5·0	6·5	8·1	10·5	13·9	17·7	23·9	30·0	37·7	46·2
64	1·2	1·6	2·2	3·0	4·0	5·5	6·5	8·2	10·9	14·0	18·7	23·9	30·3	37·4
66	1·1	1·4	1·8	2·5	3·5	4·5	5·4	6·5	8·9	11·5	15·2	19·1	24·2	30·3
68	...	1·2	1·5	2·1	3·0	3·8	4·5	5·4	7·2	9·5	12·3	15·4	19·4	24·4
70	...	1·0	1·3	1·8	2·5	3·3	3·8	4·4	5·9	7·5	9·5	12·1	15·5	19·8
72	...	...	1·0	1·4	2·0	2·8	3·2	3·6	4·8	6·0	7·5	9·5	12·0	15·4
74	...	...	...	1·2	1·7	2·1	2·6	3·1	3·9	4·9	6·0	7·5	9·5	12·1
76	...	...	...	1·0	1·4	1·8	2·1	2·5	3·0	4·0	4·8	5·9	7·5	9·5
78	...	...	...	...	1·1	1·4	1·7	2·1	2·4	3·0	3·5	4·0	5·7	7·5
80	...	...	...	...	...	1·1	1·3	1·6	1·9	2·4	2·9	3·8	4·1	5·0
82	...	...	...	...	...	...	..	1·1	1·4	1·7	2·0	2·3	2·7	3·2

* Sorel. For complete data see the volume of this work dealing with Sulphuric Acid. Sorel's data have been criticised by Porter (*Trans. Faraday Soc.*, 1913, **13**, 378), and are probably not very accurate, but they agree fairly well with Regnault's (the only others in this range). They were obtained by an air-bubbling method which justifies their selection for calculations on gas-washing.

If w = grams of water in 1 cb.m. air at $t°$ C., and h = tension of aqueous vapour (in mm. of mercury), then—

$$w = 1.060\,h/(1 + 0.003665\,t).$$

*Solubility of Sulphur Dioxide in Sulphuric Acid at 20° C.**

Per cent. H_2SO_4.	Grams SO_2 dissolved by 100 gm. Acid.	Per cent. H_2SO_4.	Grams SO_2 dissolved by 100 gm. Acid.	Per cent. H_2SO_4.	Grams SO_2 dissolved by 100 gm. Acid.	Per cent. H_2SO_4.	Grams SO_2 dissolved by 100 gm. Acid.
55·1	5·13	80·2	3·12	88·1	2·90	95·5	3·69
59·6	4·90	82·5	2·99	90·8	3·10	95·6	3·77
61·6	4·82	84·2	2·88	92·8	3·21	96·5	3·83
68·9	4·16	85·3	2·83	93·7	3·27	98·0	3·93
74·1	3·63	85·8	2·80	94·0	3·31	98·5	4·03
78·3	3·23	86·5	2·82	94·6	3·50	...	...

* Miles and Fenton, *J. Chem. Soc. Trans.*, 1920, **117**, 59.

Solubility of Sulphur Dioxide in Sulphuric Acid of Sp. Gr. 1·84.†

t°C.	11·1	17·1	26·9	42	50·9	62·3	84·3
Grams dissolved by 100 grams of acid . . .	5·26	4·35	3·0	1·91	1·47	1·12	0·71

† Dunn, *Chem. News*, 1882, **45**, 270.

CHAPTER VII

THE ABSORPTION OF SULPHUR TRIOXIDE

THE absorption of the gaseous sulphur trioxide from the gas leaving the converters is a problem presenting many points of interest and difficulty. Of the total gas volume, from 5 to 8 per cent. consists of trioxide. To effect combination with water directly is practically impossible, for the acid mist thus formed resists the most vigorous scrubbing; if such a procedure were attempted it would only become effective when the absorption had increased the concentration of the absorbing liquid, however slowly, to the region of 96 or 98 per cent. H_2SO_4. Acid of about 98·5 per cent. H_2SO_4 is the best absorbent, and is very rapid and complete in action so long as its concentration is maintained at this figure. The temperature of absorption is also important, and to control it the very considerable heat development due to the combination of sulphur trioxide with water, or with sulphuric acid, must always be taken into account. In the ensuing discussion these points will be taken *seriatim*.

THE PHENOMENA OF ABSORPTION.

Influence of Concentration of the Absorbing Acid.—Although the extraordinary fact that sulphuric acid of nearly 98 per cent. was necessary to secure the best extraction of the trioxide from the gas mixture was probably known to certain other manufacturers before that date, it was first made common knowledge by the *Badische* Company in 1901. In a British patent of that year (B. P. 6829 of 1901) a claim is made for the use of acid from 97 to 99 per cent. H_2SO_4, and Knietsch, in his first paper, stated that the absorbing power of acid

of this concentration is so great that a rapid stream of gas can be completely freed from trioxide by passage through a single absorbing vessel, provided the concentration of the absorbing acid is kept constant by a continual addition of water or diluted sulphuric acid.

These facts are of fundamental importance, and although absorption systems are arranged in many different ways, and often make partial use of acid of greater strength, the employment of this acid is always relied on to complete the absorption, if not to accomplish it entirely. Experience, therefore, confirms the conclusion of the Badische Company, and additional evidence of a deliberately experimental kind, which has hitherto been lacking, can be supplied from some of the results of an investigation made at Queen's Ferry during the War.[1]

The experiments were made in glass apparatus (a small model plant having given very irregular results), and the conditions were so chosen that the ratios of trioxide to other gas, of the total gas-volume to the capacity of the absorption tower, and of the weight of acid fed to the weight of trioxide absorbed, were as nearly as possible the same as on an actual plant. A current of air containing about 5 per cent. of trioxide was obtained by bubbling dried air through 20 per cent. oleum, kept at a definite temperature. By this method the presence of small amounts of dioxide was avoided. The gas was then heated to from 70° to 75° by passage through a heater and, after flowing through a T-piece, by which a sample could be withdrawn for analysis, was passed through a vertical tube packed with quartz, down which the absorption acid could be allowed to flow at a regulated rate. The tube was jacketed, so that when heated feed acid was run in its temperature could be maintained. The gas leaving the tower was led through a series of wash-bottles so that the unabsorbed trioxide could be estimated. Four bottles containing standard soda solution were used for the estimation in each case. The rate of flow of the feed acid down the tower was such that the concentration of H_2SO_4 rose during passage by about 0·5 and not more than 0·6 per cent. When the gas entered the tower with about 5 per cent. of trioxide

[1] By F. W. Linch and others.

and met the acid at 25° to 30° the following series of results was obtained :—

Initial per cent. H_2SO_4 in Feed Acid.	Increase of per cent. H_2SO_4 in Feed Acid.	Per cent. Trioxide in Entering Gas.	Per cent. Absorption of Trioxide.
100·2	0·5	5·00	98·2
99·1	0·5	5·14	99·1
98·25	0·6	5·01	99·6
97·5	0·5	5·00	99·4
96·3	0·5	5·08	99·2
94·5	0·5	5·10	99·0
94·0	0·6	5·11	98·9
92·5	0·6	5·05	98·6
91·0	0·5	4·98	98·4
90·0	0·6	5·11	97·6
85·2	0·6	5·08	93·6
80·6	0·6	5·04	89·0
75·3	0·5	4·98	82·0
71·0	0·6	5·15	72·6

These figures are shown graphically in Fig. 58, in which the degree of completeness of absorption is plotted against the initial concentration of the acid. The greatest effect is obtained with acid of about 98·3 per cent., but it is evident at this low temperature and under the conditions of the experiments (which were for several unavoidable circumstances more favourable to complete reaction than technical conditions) that the favourable range of concentration is a fairly wide one. Only with acid of less than 90 per cent. H_2SO_4 does the absorption fall below 98 per cent.

Influence of Temperature on the Rate of Absorption.—Another set of experiments was carried out, on all respects similar to the foregoing, except that the feed acid was heated to 60° to 65°, and was maintained at this temperature during absorption.

Initial per cent. H_2SO_4 in feed acid . .	98·9	98·15	97·3	94·0	90·0
Increase of per cent. H_2SO_4 in feed acid .	0·5	0·5	0·5	0·5	0·6
Per cent. trioxide in entering gas . .	5·06	5·02	4·98	5·00	5·13
Per cent. absorption of trioxide . . .	98·0	98·5	98·8	91·9	84·9

These figures also are plotted in the second curve of Fig. 58. The maximum is obtained at about the same concentration as before, but the narrowing of the range over which successful absorption can be carried out, is most striking. To give the

same result as at the lower temperature (say 96 per cent.

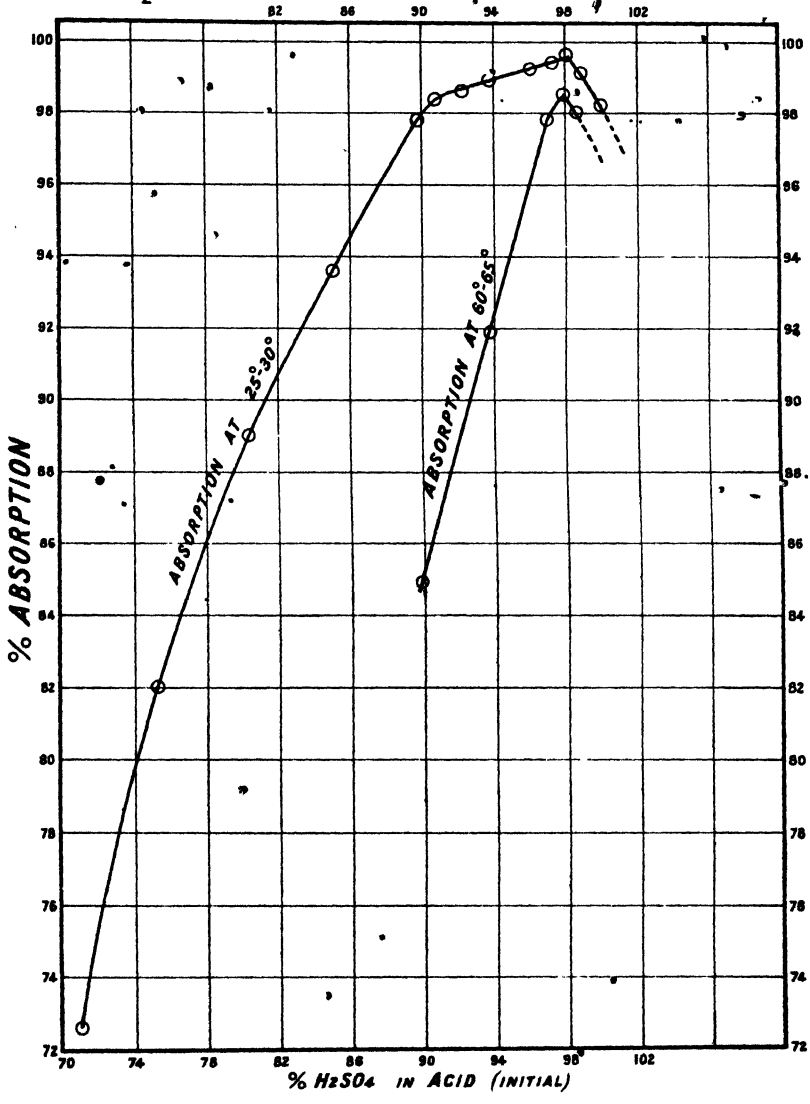


FIG. 58.—Graph connecting Rate of Absorption of Trioxide with Concentration of Absorbing Acid.

removal of the trioxide), acid of 96 per cent. must be used, whereas at the lower temperature acid of about 88 per cent.

was sufficient. In practice the conditions of the operation resemble those of the second set of experiments much more nearly than those of the first set, and it becomes clear that the higher the temperature the greater is the necessity of keeping the concentration of the active portion of the feed acid at the most favourable figure—namely, 98·3 per cent.

It will be remembered that this is also the concentration of that acid which has the highest specific gravity and the highest boiling-point (a constant one) of any of the mixtures of sulphuric acid and water, and that the vapour consists almost entirely of a mixture of water and free trioxide. It is well known also that sulphuric acid of 100 per cent. is slightly dissociated even at 18° and fumes perceptibly at 30° or 40°. Measurements of the vapour pressure of either water or sulphur trioxide at such low temperatures have not so far been made on account of the minuteness of the quantities to be measured; but it is nevertheless very probable that the vapour pressure of trioxide first becomes appreciable when the acid is about 98 per cent. in strength, and then increases more or less rapidly according to the temperature.

The application of these facts which is usually made is that due to Sackur.[1] Over acid of less than 98·3 per cent. H_2SO_4, one may suppose that a certain concentration of water vapour —however minute—could always be detected by sufficiently refined methods, and this water vapour is held to cause formation of the β modification of the trioxide, which is less readily dissolved than the α variety. It is true that the *solid* β variety has been observed to dissolve more slowly in acid than does the freshly prepared substance, but the temperature of absorption is often so high that it is difficult to suppose any solid capable of existence. This explanation is almost certainly correct in so far as it refers the inferior absorption in acid of lower concentration than 98 per cent. to the presence of water vapour, but it rests otherwise on very uncertain ground, for the polymerism of sulphur trioxide is very complex and little understood.

Sackur's theory in its original form seems to have arisen from an incomplete understanding of the facts.[2] When

[1] *Zeit. Elektrochem.*, 1902, 8, 21.

[2] See Küster, *Zeit. Anorg. Chem.*, 1904, 42, 458.

absorption is defective sulphuric acid (or oleum) mist passes from the absorbers, and not sulphur trioxide. This mist is formed by the reaction of sulphur trioxide and water vapours, just as all similar mists are formed. The water may come from the absorbing acid, if this acid is too weak, or may be due to incomplete drying before conversion, or to the leaking in of damp air. Such a mist is absorbed only slowly by acid of any strength. This fact is sufficiently difficult to explain, but no more so than similar facts in many other instances of mist-formation which are known. The peculiar property of 98·3 per cent. acid is that it has, first—a minimum vapour tension of sulphur trioxide and so is able to abstract this substance completely from the gas, and second—a minimum vapour tension of water, and so causes no mist formation.

It does not seem by any means certain that under technical conditions (where a small amount of water vapour is always present before conversion) that the trioxide comes normally to the absorbing apparatus in the condition of vapour. It may possibly be present, if the temperature is low enough, as a fine, colloidal, almost invisible mist of one of the varieties of the β substance. This "dry," as distinct from the usual "moist," mist would be absorbed best by the strongest acid.[1] The subject is a difficult one, about which very little seems to be known.

Dependence of Absorption on Vapour Pressure of Oleum.—It has been noticed that the rapidity with which sulphur trioxide is taken up by acid of about 98 per cent., is dependent on the temperature. In a far more general sense the whole of the operations of absorption depend closely on temperature, for by this factor is determined the vapour pressure of the acid and consequently not only the rate at which it can absorb trioxide, but also the total amount it can absorb. Absorption can go no further when the vapour pressure of the trioxide in the oleum equals the partial pressure of the trioxide in the gas. Take, for instance, that section of an absorption system in which 20 per cent. oleum is circulated. Referring to Fig. 5, from which may be read off the partial pressures of trioxide in any converted gas which is in equilibrium with aqueous oleum, it can be seen that if the

[1] See Remy's experiments, outlined under "Sulphuric Acid Mist."

temperature is 70°, 20 per cent. oleum can just exist in contact with a gas containing about 2·6 per cent. of trioxide. Acid of this concentration cannot under any conditions be made from a weaker gas unless the temperature is reduced, say to 50°; when a gas containing 1 per cent. would suffice, if absorption were perfectly efficient. If we fix on a trioxide percentage of 6, it is evident that to produce oleum of 45 per cent. the absorbing acid must not be above 35° in temperature, whereas if it is allowed to rise to 90°, 13 per cent. oleum is the strongest that can be made. It is on considerations of this kind that the interaction of the various parts of an absorption system can be explained and regulated, and the matter will accordingly be taken up again in connection with such systems.

The Thermal Effects of Acid-Mixing and of Absorption of Trioxide.

In connection with the absorption systems of oleum plants, it is often useful to possess fairly exact knowledge of the heat generated by the combination of the trioxide with the absorbing acid. This process is usually carried out in more than one stage, and acid may be transferred from one section of the apparatus to another in which the concentration of the circulating acid is higher. In this case also heat is developed to an extent which is dependent on the concentrations of the two acids which are mixed. For these reasons, and also in order that calculations may be carried out for other purposes, it is advisable to have ready means of finding (A) the heat development due to mixing two quantities of acid or oleum of any two concentrations; and (B) the heat due to the absorption of gaseous sulphur trioxide in acid of any given strength. Given acids of two different concentrations—suppose an acid of a per cent. H_2SO_4 and an oleum of b per cent. H_2SO_4—some arithmetic is first necessary to find first of all either the proportion in which they must be mixed to give a final acid of c per cent., or the concentration (c) which will result by mixing in a given proportion. If, as may often be the case, problems of this kind have frequently to be carried out, a number at a time, a simple graphical method is of use. Such a method is supplied by the chart of Fig. 2.

(A) *Calculation of the Heat of Mixture.*—The most complete data are those given by Porter.[1] It is convenient, in dealing with oleum, to refer the calculations to unit weight of water present. The heat evolved (in calories or C.H.U.), when unit weight (one grain or pound) of water is mixed with m times its weight of trioxide at a temperature $t°$, will be denoted by k_t. It has already been explained how these values of k_t can be obtained from Knietsch's figures for the heat of solution of oleum (see Heat of Solution of Sulphur Trioxide), and a number of equations by means of which, for several ratios of trioxide to water, the results can be adjusted for various temperatures, have already been given. Below are values at selected temperatures, found from the equations mentioned. The figures in the first column relate to the concentration after mixing the sulphur trioxide and water.

Heat of Mixture of Sulphur Trioxide (Liquid) and Water (1 Gm.)

Per cent. Total SO_3	k_t – (Cals. or C.H.U.).				Difference for 10°.
	0° C.	50° C.	100° C.	150° C.	
81·63	1176	1302	1429	1556	25·4
85·00	1206	1364	1522	1680	31·6
90·00	1293	1502	1711	1920	41·8
95·00	1479	1750	2021	2292	54 2
98·00	1605	1911	2217	2523	61·2

The greater (and more generally useful) part of this table is shown in the form of graphs in the lower half of Fig. 59, from which the value of k_t for each 25° between 0° and 100° may be found at a glance with a precision sufficient for the general purposes of design. These figures apply only to oleum. A corresponding set is necessary for acid of less than 100 per cent. These can be deduced from the various values of the heat of dilution of sulphuric acid determined by Pfaundler and by Bronsted, combined with the heat of reaction between sulphur trioxide and water determined by Thomsen—

$$SO_3(\text{liq.}) + H_2O(\text{liq.}) = H_2SO_4(\text{liq.}) + 21.300 \text{ cals.}$$

[1] *Trans. Faraday Soc.*, 1917, **13**, 373.

A selection of such data is given in the table below:—

Heat of Mixture of 1 *gm. Water with Trioxide (Liquid).*

Per cent. Total SO_3.	Per cent. H_2SO_4.	k_t (Cals. or C.H.U.).			Difference for 10°.
		0° C.	50° C.	100° C.	
50·0	61·2	410	444	477	6·7
55·0	67·4	483	524	564	8·1
60·0	73·5	565	614	663	9·8
70·0	85·7	778	851	924	14·6
73·5	90·0	872	955	1039	16·7
74·3	91·0	896	982	1069	17·3
75·1	92·0	919	1009	1099	18·0
75·9	93·0	944	1038	1132	18·8
76·7	94·0	970	1068	1166	19·6
77·6	95·0	996	1108	1200	20·4
78·4	96·0	1024	1129	1235	21·1
79·2	97·0	1053	1163	1273	22·0
80·0	98·0	1081	1195	1310	22·9
80·8	99·0	1113	1232	1352	23·9
81·63	100·0	1146	1270	1395	24·9

These figures are also given in graphical form in the upper half of Fig. 59.

Example 1.—To continue the example quoted on p. 43 in connection with the mixing chart, suppose that 500 lb. of 30 per cent. oleum are mixed with 90 per cent. acid to give 96·7 per cent. acid. What heat will be developed if the mixture takes place at 50°?

The weight of 90 per cent. acid used will be $500/0.667 = 750$ lb.

From the tables on pp. 41 and 42—

(*b*) 500 lb. 30 per cent. oleum (87·1 per cent. SO_3) contain 65 lb. H_2O.
(*a*) 750 „ 90 „ acid (73·5 „) „ 199 „
(*c*) 1250 „ 96·7 „ „ (78·9 „) „ 264 „

Finding k_{50} from the graphs, we calculate in each case the heat of formation of the acid from 1 lb. H_2O. The difference between the sum of heats of formation of the 500 lbs. of oleum and the 750 of 90 per cent. acid, and the heat of formation of the 1250 lb. of 96·7 per cent. acid, is the result required,

(*b*) Oleum . . $k_{50} = 1410$. Heat of formation $= 65 \times 1410 = 91{,}650$ C.H.U.
(*a*) 90 per cent. acid „ $= 955$. „ „ $= 199 \times 955 = 190{,}520$ „
(*c*) Resulting acid „ $= 1150$. „ „ $= 264 \times 1150 = 303{,}600$ „

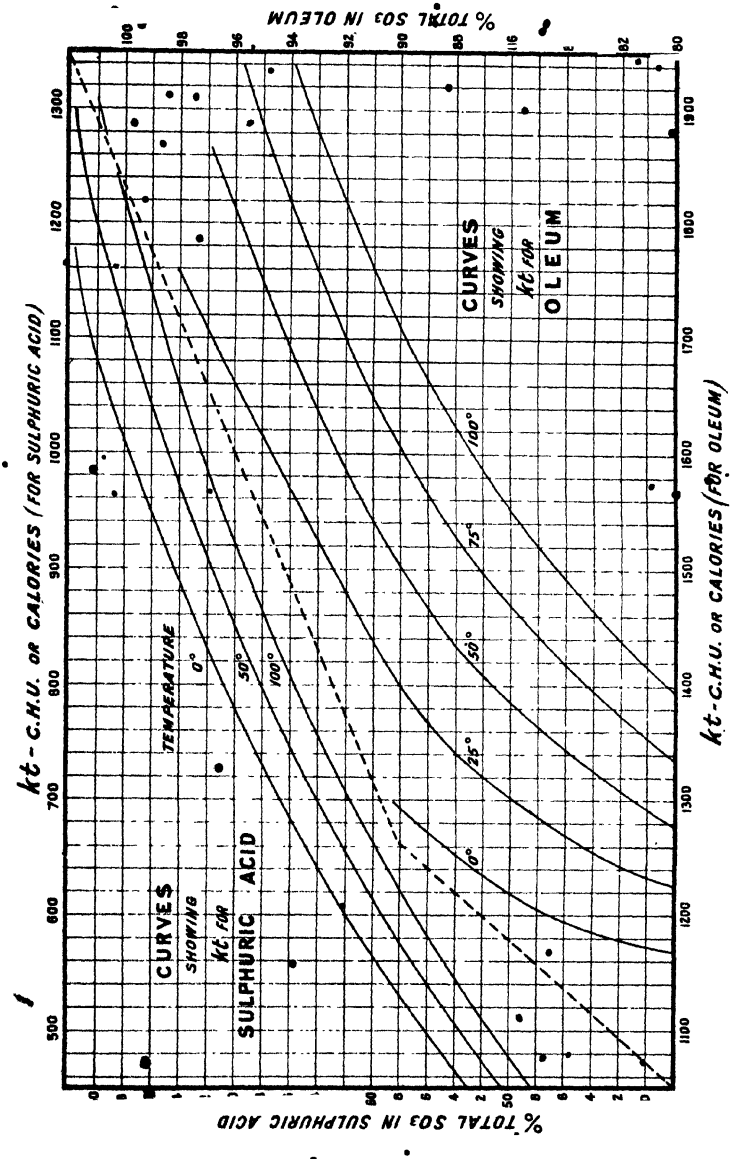


FIG. 59.—Heat of Mixture of Sulphur Trioxide and Water.

so that the heat of mixture = 21,430 C.H.U., *i.e.*, roughly, sufficient to raise the temperature of the mixture by about 49° (taking sp. ht. = 0·35).

Example 2.—Oleum of 20 per cent. free trioxide is "broken down" with water to 98 per cent. acid. If both acid and water are initially at 25°, what will be the temperature of the mixture?

1 lb. 98 per cent. acid (80 per cent. SO_3) contains 0·80 lb. SO_3 and 0·20 lb. H_2O, and in 20 per cent. oleum (85·3 per cent. SO_3), 0·80 lb. SO_3 are associated with 80 × 14·7 / 85·3 = 0·138 lb. water. Then, from the data given,

(*b*) Oleum. $k_{25} = 1290$ C.H.U.
Heat of formation = 0·138 × 1290 = 178 C.H.U.

(*c*) Acid 98 per cent. $k_{25} = 1138$ C.H.U.
Heat of formation = 0·20 × 1138 = 228 C.H.U.

so that the heat of dilution from 85·3 to 80 per cent. total SO_3 = 228 − 178 = 50 C.H.U. per lb. acid obtained. The specific heat of 98 per cent. acid is 0·35, so that the rise in temperature will be 50 / 0·35 = 143° C.

(B) *Calculation of the Heat of Absorption of Gaseous Trioxide.*—This class of calculation may be treated in the same way if allowance is made for the latent heat of condensation of the trioxide (Porter, *loc cit.*). Thus, if the heat evolved during the supposed condensation of m gm. of gaseous trioxide into 1 gm. of water at $t°$ be denoted by H_t, and k_t has the same meaning as before,

$$H_t = k_t + ml_t.$$

The quantity l_t is the latent heat of vaporisation of sulphur trioxide and is about 123 cals. per gram at 0°, 116 at 50°, and 112 at 100°. (For its derivation see the section on Sulphur Trioxide.)

In the tables which follow, the first column, as before, refers to the composition of the mixture produced by the supposed addition of trioxide to water.

The method of using this table is the same as before.

Examples.—It will be interesting to compare the thermal effects of condensing 1 lb. of trioxide, at 50°, into (3) 4 lb. of 100 per cent. acid to give 20 per cent. oleum, and into (4) 4 lb. of 95 per cent. acid to give 2·5 per cent. oleum.

Heat of Condensation of Trioxide (Vapour) in 1 $\left\{\begin{matrix} lb. \\ gm \end{matrix}\right\}$ *Water.*

Per cent. Total SO_3.	Per cent. H_2SO_4, or per cent. Free SO_3.	Ht (Cals. or C.H.U.).		
		0° C.	50° C.	100° C.
72·7	89·0	1186	1247	1318
73·5	90·0	1212	1276	1349
74·3	91·0	1251	1317	1393
75·1	92·0	1290	1359	1437
75·9	93·0	1332	1404	1485
76·7	94·0	1375	1450	1535
77·6	95·0	1421	1509	1586
78·4	96·0	1469	1548	1641
79·2	97·0	1520	1604	1699
80·0	98·0	1573	1659	1758
80·8	99·0	1631	1720	1823
81·63	100·0	1693	1785	1892
82·0	2·0	1736	1830	2060
83·0	7·5	1783	1885	2133
84·0	13·0	1839	1950	2211
85·0	18·3	1903	2023	2296
86·0	23·8	1982	2106	2395
87·0	29·3	2070	2205	2509
88·0	34·7	2170	2311	2633
89·0	40·1	2280	2424	2763
90·0	45·6	2400	2548	2898

(3) 4 lb. 100 per cent. acid (81·63 per cent. SO_3) contain $4 \times 0{\cdot}1837 = 0{\cdot}735$ lb. water.

For 100 per cent. acid, $H_{50} = 1785$. Heat of formation $= 0{\cdot}735 \times 1785$ C.H.U.
For 20 per cent. oleum, $H_{50} = 2048$. Heat of formation $= 0{\cdot}735 \times 2048$ C.H.U.

The difference between these two quantities is 193 C.H.U.—the result required.

(4) 4 lb. 95 per cent. acid (77·6 per cent. SO_3) contain $4 \times 0{\cdot}224 = 0{\cdot}896$ lb. H_2O. Addition of 1 lb. SO_3 raises the SO_3 concentration to 82·4 per cent.

For 95 per cent. acid, $H_{50} = 1509$. Heat of condensation $= 0{\cdot}896 \times 1509 =$ 1352 C.H.U.
For the final acid, $H_{50} = 1836$. Heat of condensation $= 0{\cdot}896 \times 1836 =$ 1645 C.H.U.

and the heat development of the charge is therefore 293 C.H.U.

These two results are of interest in that they show the thermal effect of absorption, above 100 per cent. H_2SO_4, to be

considerable in comparison with effect below 100 per cent., where (for the most part) free water is present. The reason is, of course, that the abstraction of the free water from the sulphuric acid, with which it is associated in some very intimate way, involves a large *absorption* of heat, by which the apparent energy of the chemical combination between trioxide and water is reduced.

Absorbers and Adsorption Systems.

The object of the absorption process being the complete removal of the vapour of sulphur trioxide from the converter-gas, the means which are available do not differ essentially from those used in any other process of gas-washing. Absorption may therefore be carried out in (1) surface absorbers; (2) bubbling apparatus in which the gas is forced below the surface of the absorbing liquid and allowed to rise through it in bubbles; and (3) packed absorption towers. In each case the chemical and physical changes occur mainly, at the surface where gas and liquid meet, and the absorbers of class (1) are therefore not exceptional, their only difference from the others lying in the fact that a plain surface of liquid, at rest or in slow motion, is relied on.

(1) *Surface Absorbers.*—This type of apparatus was fitted to many of the older plants of the Grillo type, and is still occasionally used. Owing to the comparatively small surface, it is generally confined to the first stage of absorption—the actual production of oleum. The absorber often consists simply of a cylindrical vessel with its axis horizontal, fitted with inlet and exit connections for the gas, entirely or mainly above the acid level. The acid enters at one end of the cylinder and leaves at the other, passing in counter-current to the gas stream which is projected against the liquid surface by means of baffle-plates. The absorber is cooled by running water over it, or sometimes by entire immersion in water. This type of apparatus has been fitted to the plants built by the Simon-Carvés Company in this country, at the Dalton Works of the British Dyestuffs Corporation.

Another instance, illustrated in the sketch of Fig. 60 is described by Pascal.[1] In this case the steel shell, 1·5 metre

[1] *Synthèses et Catalyses Industrielles*, 1921, ii., 83.

in diameter and 5 metres long, is lined with 8 cm. of acid-proof brick. In the middle is a 25 cm. wall of volvic stone in which are arranged, by the insertion of special stones, twelve diamond-shaped perforations through which the gas can pass

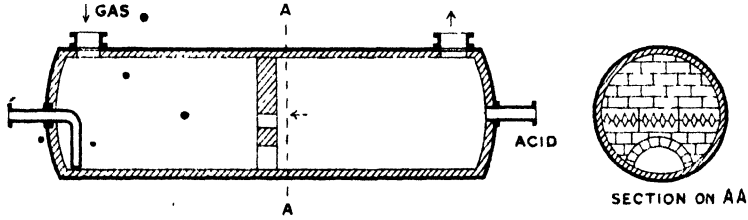


FIG. 60.

in close contact with the liquid. In the base of the wall is a lens-shaped opening of 60 cm. diameter. Acid passes into the absorber at one end and out at the other.

Oleum can be produced in absorbers of this type up to 45 or 50 per cent. of free trioxide.

An absorber in which the gas-space is restricted to bring liquid and gas more closely into contact is that illustrated in Fig. 61, and described in one of the Herreshof patents. (Herreshof and the General Chemical Company, U.S. Ps. 722981 and 737233 of 1903). It consists of a long cast-iron vessel standing in a cooling jacket. The absorbing acid enters at one end at the bottom and passes out at the other end from the top. The top of the vessel is made in the form of a tray, in which cooling water can be contained.

(2) *Bubbling Absorbers.*—This form of apparatus is similar in construction to the gas-scrubbers which have been described and illustrated. A single absorber usually consists of a cylindrical steel vessel with its axis vertical, surrounded by a water-jacket. In the vessel is placed a steel or cast-iron dome with serrations round the bottom edges or with concentric rows of holes below the acid level, or with both provisions. The gas is led into the dome and escapes into the absorbing acid through the holes or serrations, and is thus brought into intimate contact with the acid. Instead of a dome a ring-shaped steel pipe has been used, and in some cases the cylindrical absorbing vessel has been

placed with its axis horizontal, the gas being led into a long perforated steel pipe placed about 10 cm. below the acid level.[1]

This is undoubtedly a very efficient method of absorption

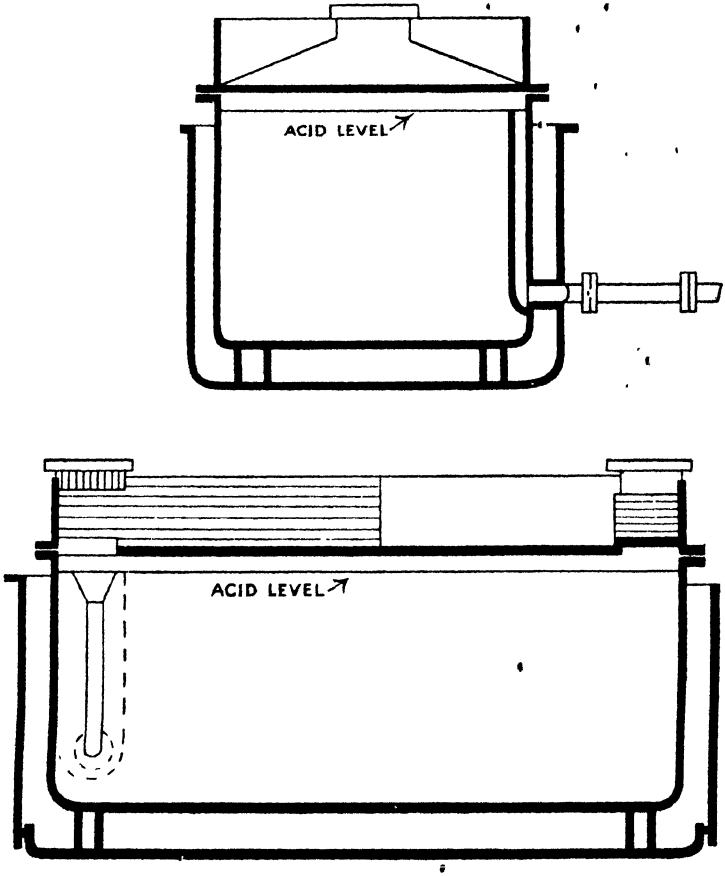


FIG. 61.—Surface Absorber.

but, as in all similar methods of scrubbing, the existence of a head of liquid through which the gas must be forced, involves the use of additional power. In this case the head is large, owing to the high density and viscosity of the acid, and the substitution of towers of large capacity (the initial cost of

[1] Pascal, *loc. cit.*

which is high) for the smaller absorbers, is somewhat less expensive than it appears at first sight.

Illustrations of the general outlines of an absorber will be found in Fig. 114, where the apparatus in use on Tentelew plants is represented. The acid enters the absorber at the bottom and flows out of it from the top. In an installation comprising two absorbers we have, then, sulphuric acid of say 90 per cent. entering No. 2, in which, by the addition of the last fraction of trioxide from the gas, the contents are kept at nearly 98 per cent. H_2SO_4. This acid then overflows into No. 1, in which the contents are constantly kept at the strength of 20 per cent. oleum, by the addition of the first fraction of trioxide abstracted from the gas. The overflow from No. 1 is the make of 20 per cent. oleum.

If such apparatus as this is urged to its maximum capacity, the cooling becomes a serious problem, for it is obvious that the fraction of the trioxide which is retained by the 20 per cent. oleum will depend on the vapour tension of the trioxide due to that liquid and consequently on the temperature. This point will receive more detailed treatment below; for the present it is sufficient to emphasise the necessity of temperature control. The external cooling of large vessels is never a very efficient process, and for plants of large capacity separate coolers are generally preferred. A proposal to increase the cooling facilities in an absorber of this type has, however, been made (Herreshof and the General Chemical Company, *loc. cit.*) in an American patent. The sketch of Fig. 62 illustrates this. Instead of the bell with serrations there is an extension of the bell into an annular plate with numerous holes, and above the holes is arranged a special steel coil through which cooling water is passed. Cold acid runs in at the bottom and passes out from above the bell. The cooling is applied just where the heat is generated.

Plant has also been constructed in which several of these absorbers were combined, although it does not appear to be in general use. The Tentelew absorbing tower (B. P. 22095 of 1907) is shown in Fig. 63 in vertical section, and also half as seen externally from the top and half in horizontal section. Three or more chambers, a_1, a_2, a_3, are superposed on one another. Each contains a specially shaped gas-entrance

pipe *b*, surmounted by a dish *c*, which is tightly connected with the sides of the chambers, and provided with a perforated margin, *d*. The gas is thus compelled to spread equally over the horizontal section of the tower. Fig. 63 shows the "staggered" arrangement of the holes, which causes a very intimate contact between the gas and the liquid, so that the gas bubbles are prevented from flowing together and

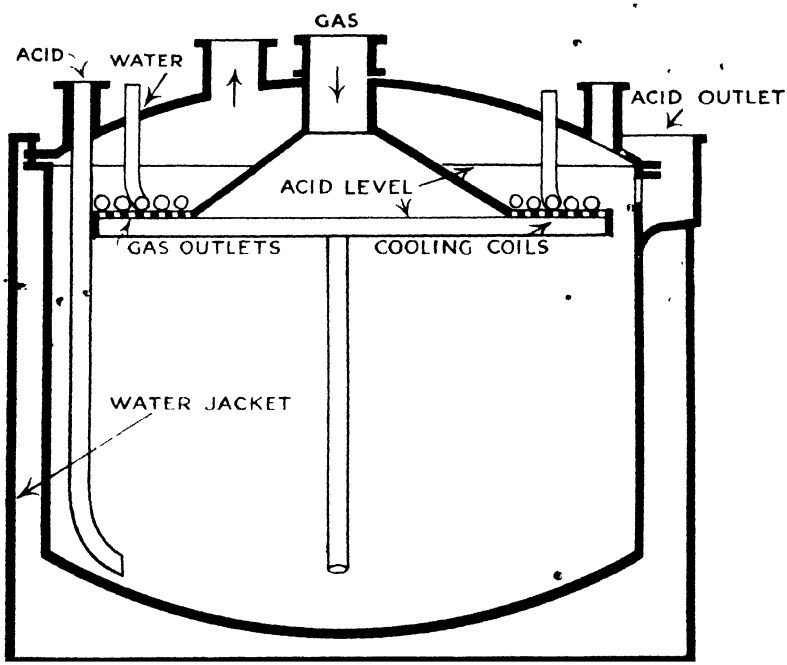


FIG. 62.—Absorber with Internal Cooling.

coalescing. This produces very good absorption, and is said to allow of the head of liquid being decreased. Each chamber is surrounded by a cooling jacket, and the cooling is promoted by arranging the perforated zone of the bell at such an angle to the sides of the chamber that the liquid is thrown outwards against the cool walls in the direction of the arrows. In the top-chamber, the pipe *b* projects higher up from the liquid than in the lower chambers, so as to facilitate the absorption of the last portions of the gas. The finer the holes, the better

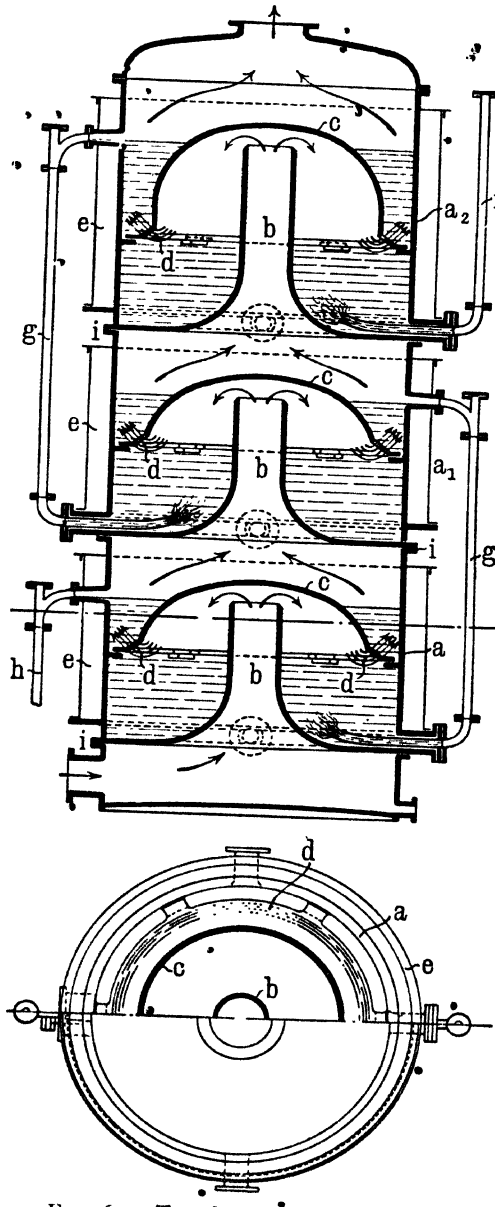


FIG. 63.—Tentelew Multiple Absorber.

is the division of the gases, and the quicker the absorption. The total clear space of the holes is best made equal to that of the exit opening of the pipes *b*. The sulphuric acid, serving for absorbing the gas, is either introduced near the top at *f* and flows through all the chambers by means of the connecting pipes *e* ultimately running-out at *h*, or each chamber is provided with a separate inlet and outlet for the acid. As single absorbers often have to be cooled not only at the sides but at top and bottom as well, the efficient cooling of such plant as this cannot be easy. Although the arrangement is compact, the sections are not independent, so that repair, rearrangement of operation, and alteration of connections, would be simpler with separate sections.

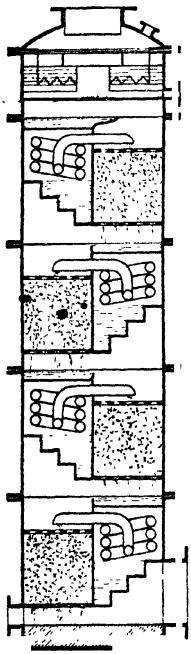


FIG. 64.

Another proposal (vom Hofe, Ger. P. 166599) may be noted here, for although the use of packed absorbing sections is mentioned in it, the sections are superposed one on another. Each compartment is divided by an internal plate, in such a way that one side forms a cooling chamber with a stepped bottom and a cooling coil, and the other an absorbing chamber. The general arrangement is shown in Fig. 64. The acid enters at the top and passes over the cooling-coils and packing alternately. The objection in point of complication would seem to apply to this in double measure.

(3) *Packed Absorption Towers.*—Absorption towers ar usually constructed with a shell of steel, but sometimes th shell is cast-iron. It is usual and preferable to line the with acid-resisting brick set in a suitable cement, for n only does this lengthen the life of the tower but th troubles due to formation of sludge—blocking of the tower an contamination of the acid—are made very much less. A goo example of this construction may be seen in Fig. 93, p. 31 which represents the type of tower used in H.M. Factori during the War, as well as in many others now running. Th

steel shell of the tower (about 24 ft. high by 6 ft. diameter) is closed at the top with a flat steel cover. The acid is pumped into the tower through a sight-box and passes to the packing by way of a cast-iron distributing plate.

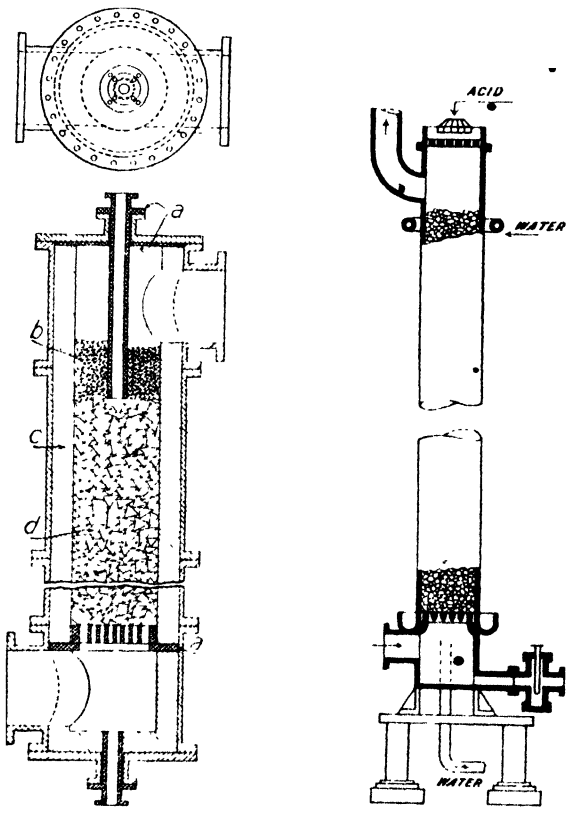
The packing consists of graded quartz about 4 or 6 in. long. Granite is sometimes used, but is inferior on account of its slight tendency to be corroded and to give rise to sludge. The weight of the packing, and of the iron grid in which it rests, is borne on a central cast-iron pillar, the base of which rests on the bottom of the saucer.

The gas is generally passed in at the bottom of the tower and out at the top, so that its direction is opposite to that of the acid. This is considered to be the proper way, although it involves long and rather cumbrous gas connections from the top of one tower to the bottom of the next. In some cases where the load on the plant is only moderate—as in the usual Mannheim installation, shorter connections—from top to top and from bottom to bottom—have been fitted without causing any notable difference in the result.

Efficient absorption in such large towers as this is largely dependent on maintaining a constant stream of acid over every part of the quartz, especially when the plant is carrying a heavy load. Rarely, if ever, is the acid simply run once through the tower and then removed from the system, as with the two previous types of absorber, although in some plants in this country at least, the experiment has been successfully made. For each tower or pair of towers a tank is provided, and the acid is thrown up from this tank to the sight-box of the tower by a pump and then returns to the tank, usually through a cooler in which the heat of absorption is removed. From this system a smaller amount of acid is continuously removed, fresh acid entering to take its place. To obtain the maximum work, for instance, from towers of the size given, a feed of 10 tons of acid per hour to each tower is by no means excessive. The weight of sulphur trioxide absorbed in a single tower in the same time can hardly exceed 0·25 ton, so that the acid removed from the system will be in any case very much less than the feed.

American practice appears to be different. In some plants the gas is passed through a number of towers arranged in

series, each at a higher level than the next. The absorbing acid passes down each tower in succession and is removed as oleum from the last. The strength of the oleum made is regulated by the amount of the acid supplied. Such towers may be of 15 in. to 30 in. inside diameter and 10 ft. to 25 ft.



(a) (b)

FIG. 65.—Packed Absorbers—American Practice.

high, and may be constructed with steel shells and cast-iron bases and tops. The shell is lined with cast-iron liner-rings or sections, the narrow space between shell and rings being filled with an acid-proof cement which hardens in use. A tower of this kind is shown in Fig. 65 (*a*), but the lining in this case is acid-proof brick.[1] In the figure, C is this lining, the acid-feed pipe and the lower ring and grid (*a*) are tantiron.

[1] *U.S. Dept. of Int., Bull.*, 1920, **184**, 189.

The upper packing (*b*) is 3-in. quartz, and the lower packing 4-in. quartz. In Fig. 33 is shown a battery of three such towers in an American installation built on the lines of the *Badische* plant. Fig. 65 (*b*) shows somewhat similar tower, so built that the whole external surface can be cooled by water.[1] The radius of the cylindrical body must not exceed 7 in. For each cubic inch of effective space there should be $\frac{1}{3}$ sq. in. of external cooling area. From these dimensions, adherence to which is stated to be of great importance, it follows that the height of the tower equals eleven times its diameter. The packing consists of quartz pebbles.

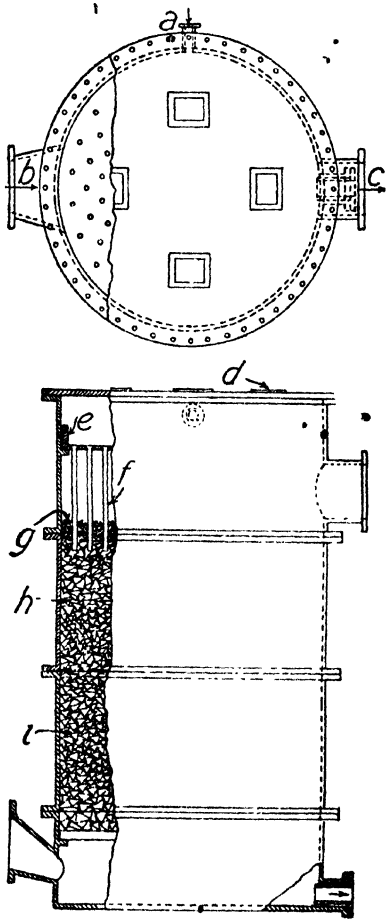


FIG. 66.—Final Absorber—American Practice.

Instead of these towers being arranged in series, several may be supplied with gas by parallel pipes from a common header. The volume of gas entering each tower is regulated by a valve. Whichever system be adopted the gases leaving the towers must be passed to other absorption apparatus for the abstraction of the trioxide they still contain.

The final absorber is often of the type shown in Fig. 66. This is of cast-iron. The gas-inlet at the bottom is set at an angle to prevent acid flowing into the pipe. The gas-outlet is either at the top or at the side close to the top. There is a grid of cast-iron set in the bottom saucer, and on this is

[1] Briggs and Merriam, U.S. Ps. 1013 68 and 1083012.

placed a packing of quartz pebbles or specially made acid-proof material, to a depth of several feet. In the sketch *g* is fine quartz, *h*, 3-in., and *i*, 6-in. quartz. The acid is run into a distributing pan *e*, set in a flange in the top ring, and runs down through a number of porcelain tubes *f*, which are cemented into the plate at their upper ends. These tubes are from $\frac{1}{4}$ to $\frac{3}{8}$ in. in bore and extend to below the top of the packing. Glass panes (*d*) allow of inspection and of opening for cleaning out the tubes.

This pattern of tower is often used, not only for final absorption, but also for drying the gas before conversion, and two towers having these separate functions are often fed with acid by a pump drawing from a single tank.[1]

From packed absorption towers, as also from other types of final absorbers, acid spray is liable to be carried away and to cause nuisance and loss. This has been overcome by a variety of devices. Spray-catching chambers constituting simply an enlargement of part of the outlet pipe have been used, and the design of the centrifugal steam and water separator has been copied. It would probably be advisable to set the distributing plate of the last of a series of towers lower down in the tower than usual, and so leave a space above through which the gas ascended with reduced velocity. The Cottrell apparatus is also working in the United States for the collection of the mist and acid particles which the absorbers fail to retain. It should be remarked, however, that a well-designed absorption system leaves little to collect, of either mist or spray.

Arrangement of Absorbers.—The number of the absorbers that are required and the method of connecting them depend on the size of the plant, the nature of the acid being made, the efficiency of the coolers, and the strength of the feed. If 20 per cent. oleum is to be produced, as we shall very generally assume, the feed may be water, dilute acid from the drying towers or from external sources, or acid recovered from the waste acid of nitration processes and reconcentrated by evaporation to 94 per cent., or to some other figure decided on to suit the economy of the works of which the sulphuric acid plant is a constituent part.

Since 20 per cent. oleum can be made by one passage of

[1] *U.S. Dept. of Int., Bull.*, 1920, 184, 164.

the converted gas through or over acid of very nearly this strength, and since the remaining trioxide can be absorbed by passing it once (or perhaps twice) through or over sulphuric acid of nearly 98 per cent., there is no need for the acid in any tank in the absorption system, or in a pump or connecting pipe, to depart very much from one or the other of these two concentrations. The presence of intermediate strengths of weak oleum is to be avoided not only on the grounds of simplicity, but also because the corrosion of iron and steel is increased as the concentration of 98 per cent. H_2SO_4 is exceeded, and reaches a maximum with about 10 per cent. of free SO_3.

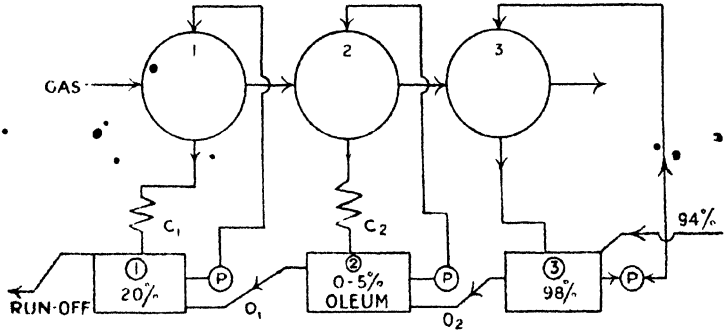


FIG. 67.—Absorption System for making 20 per cent. Oleum—Three Different Circulating Acids.

In many systems, however, this principle has not been adopted. Suppose, for instance, that there are three towers through which the gas is passed in succession, and that acid from three tanks is circulated round the towers. If 94 per cent. acid is fed in and oleum removed, the state of affairs will be that shown above.

The 94 per cent. acid enters tank No. 3 in quantity sufficient to prevent the absorption in tower No. 3 from strengthening the acid to more than 98 per cent. C_1, C_2 are coolers. By means of the connections O_1, O_2, acid is constantly overflowing from one tank to the next. As a matter of fact, with these arrangements it is by no means an easy matter in many cases to secure that 98 per cent. acid is present in tank No. 3 and 20 per cent. oleum in No. 1 at the same time; but if they are, No. 2

tank contains an acid which is neither, and depends in strength on the fractions of total absorption which occur in all three towers as well as on other factors.

Suppose, now, that the middle tank and pump be removed, and the last two towers connected to the third tank. A more rational arrangement at once results.

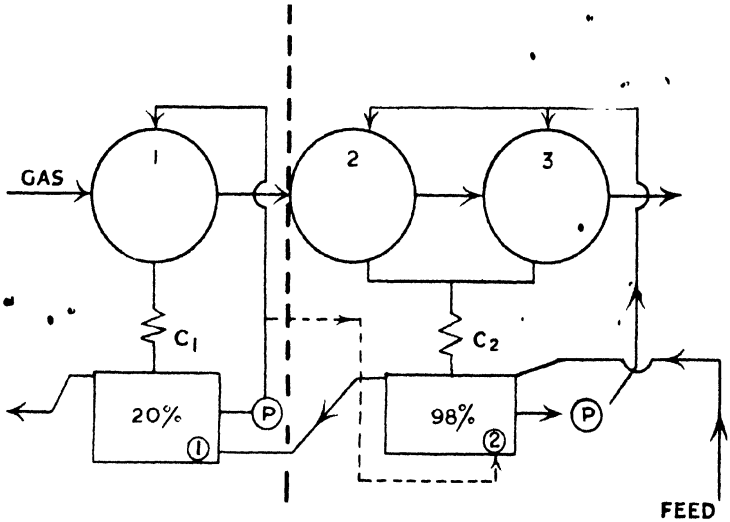


FIG. 68.—Absorption System for making 20 per cent. Oleum—Improved Type with Two Circulating Acids.

Two kinds of acid only are in use, and the system can readily be considered in two parts, the "oleum section" and the "98 per cent. acid section." Experience with this arrangement on large plants shows that it is advantageous to construct in steel the connecting pipes and the large coolers which are necessary for heavy loads, in the first section, and to use cast-iron for the corresponding parts of the second (or 98 per cent. acid) section. Cast-iron cannot be used for oleum without cracking, but resists concentrated acid, if the temperature is not too high, better than does steel.

This system deserves more detailed consideration. We may replace the towers by other absorbers, or dispense with the circulating pumps—as when using the Tentelew apparatus or surface absorbers—without essential alteration, although

the possibility of modification may be very much diminished by substituting other plant. We may suppose that .90 per cent. acid is being used as feed. From the table on p. 276 can be found at once the amount of feed of any strength above 85 per cent., which is required to absorb 1 ton of trioxide, and to produce either 98 per cent. acid or 20 per cent. oleum. Considering first the 98 per cent. acid section, it is seen that 3·06 tons of feed acid are required and the result is 4·06 tons of 98 per cent. acid. As regards the oleum section 2·77 parts of this acid absorb 1 ton of trioxide, or 4·06 tons absorb 1·47 tons. Of all the trioxide absorbed, therefore, 40 per cent. is retained by the 98 per cent. acid and 60 per cent. by the oleum. This percentage of absorption in the first tower of a series—of about 60—is a very usual one; but it may be exceeded with ease, if the temperature in the tower is low enough and the acid feed is sufficient. On the other hand, with acid which is too hot or insufficient in amount, it may not be reached. In either case the balance of the two systems is then upset, and either, in the first case, the oleum in No. 1 tank becomes too strong when the feed is regulated to keep No. 2 at the right strength, or, in the second, so much 98 per cent. acid has to be made in No. 2 that it cannot be sufficiently concentrated in No. 1. If the conditions are such that the absorption is divided between the two sections in the right ratio to begin with, the plant may run well, but the problem of securing a balance of the two sections is in general a trouble.

Several modifications can be, and often have been, introduced to give a greater facility of adjustment. There can be little doubt that the simplest would be to control the temperature, and therefore the absorption, in each section separately, in accordance with the argument of pp. 277-279. The usual cooling arrangements, however, have not permitted this control. Another way is to divide the entering stream of feed into two parts, and to add one to each system. The overflow from No. 2 to No. 1 tank proceeds as usual. This works well, and when constant conditions have been established goes on without attention, particularly if some form of meter is employed to fix the rate of flow in each case. Such a meter may be of the notched weir type, or may consist of a rectangular box divided

into two by a diaphragm perforated with holes. Fig. 69 illustrates a meter of this latter kind. The feed is run into one side of the steel box and finds its way into the other, from which it is run off for use, by means of the holes in the diagonal plate. The flow may be fixed by adjusting the supply valve until any desired number of jets are issuing from the holes.

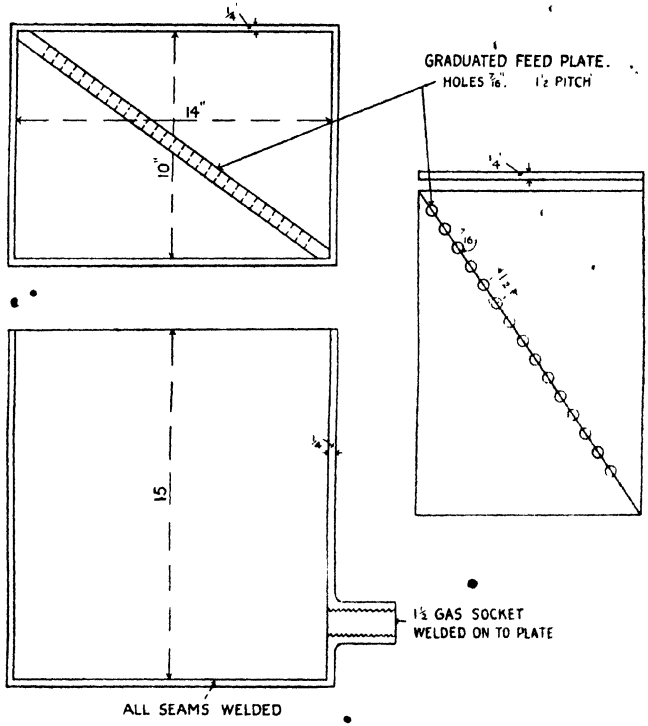


FIG. 69.—Feed-Box for Acid.

Another method of assisting the balance of the sections is to provide for transfer of acid from No. 1 to No. 2. Usually the acid in No. 2 requires reinforcing, and this has often been done by connecting the rising main of the pump on the No. 1 side to the tank on the No. 2 side. Such a connection is indicated in Fig. 68 by the dotted line. This procedure can be made to go well, but the regulation of a stream of oleum is less simple than that of a stream of feed acid or water, and the

volume of the stream is very much greater. The first method is therefore preferable. It should be noted that if the adjustment required were in the other direction, *i.e.*, if the absorption in No. 2 section were too complete, that in No. 1 being too low, this method of acid transfer could not be employed. In this event either more dilute feed acid would have to be used, or

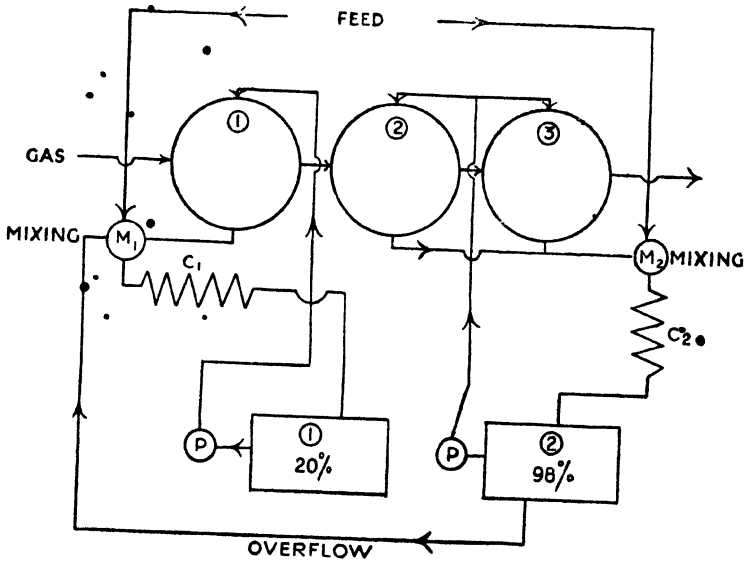


FIG. 70.—Absorption System for making 20 per cent. Oleum—Second Improved Type.

the proportion of absorption changed by altering the temperatures in, or the respective rates of feed to, the towers. But since the proportion of the trioxide absorbed in No. 1 tower can readily be maintained at 60 to 70 per cent., difficulty under this head does not usually arise.[1]

[1] A slight variation in operation, when no by-pass is fitted, may lead approximately to the same result. In the event of absorption in the oleum section being too high, No. 2 acid can often be strengthened by closing the run-off from No. 1 intermittently, the feed to No. 2 being continuous. In this way 20 per cent. oleum has been made from a single water feed in a system similar to Fig. 68, without any by-pass. Cutting down the feed to No. 1 tower has the same effect, *i.e.*, more trioxide passes on to where it is required.

Whichever method is adopted, the points at which the streams are to be mixed require consideration. If feed acid is to be added to oleum, for instance, it is clearly undesirable that the mixture, which gives rise to great heat development, should take place in the tank from which the acid flows to the pumps and towers, for both the life of the pumps and the completeness of the absorption may be influenced adversely. The proper place for mixture is just before the cooler, and if this principle is to be applied comprehensively, the overflow from the No. 2 tank must also be delivered at the same point. The resulting arrangement is represented by Fig. 70.

The provision for the overflow to run to the mixing aperture has not been made, so far as is known, in any of the plants on which the other modifications have been introduced, for it would involve placing the No. 2 tank and its connected apparatus at a higher level than No. 1. A connection from the rising main of No. 2 pump to the mixing junction would serve the same purpose, but the transfer would no longer be an automatic one.

Feed Acid Table.

Feed.	Tons Feed required for 1 ton SO_3, Product being			
	98·0 per cent. H_2SO_4.	98·5 per cent. H_2SO_4.	20 per cent. Oleum.	22 per cent. Oleum.
Water.	0·2500.	0·2436.	0·1722.	0·1672.
Sulphuric Acid, per cent. H_2SO_4				
85·0	1·89	1·78	0·92	0·88
86·0	2·04	1·92	0·97	0·93
87·0	2·23	2·09	1·03	0·98
88·0	2·45	2·28	1·09	1·03
89·0	2·72	2·53	1·16	1·10
90·0	3·06	2·82	1·24	1·17
91·0	3·50	3·20	1·33	1·26
92·0	4·08	3·69	1·44	1·36
93·0	4·90	4·36	1·57	1·47
94·0	6·12	5·33	1·71	1·60
95·0	8·16	6·85	1·89	1·76
96·0	12·25	9·60	2·11	1·96
97·0	24·50	16·00	2·40	2·20
98·0	...	...	2·77	2·52
98·5	...	...	3·00	2·72

The Application of Vapour Pressure Data to Control.—The description which has been given of absorption arrangements which have been or might be adopted, has assumed no more technical data than have hitherto been available. The key to the scientific analysis of the absorption problem is a knowledge of the vapour pressures of oleums of various concentrations, at various temperatures. Knietsch's figures (*q.v.*) are useless for this purpose. The recent data of M'David are now available, and it is by the same author that the method of applying them to absorption problems has been indicated. The examples quoted are given by him.[1]

It is necessary to assume that the concentration of the acid in any absorber is the same throughout the vessel, and the same as that of the acid flowing out. In a well-designed system this may be taken to be correct, even for one of the tower type, if the rate of circulation is great in comparison with the rate of "forwarding." The usual assumption that the gas leaving each absorption vessel is in equilibrium with the acid in that vessel, in regard to trioxide, can readily be accepted. In the case of a tower it will be advisable to regard the temperature in the region of the gas-outlet as the equilibrium temperature. Further, in order to apply the results to practical work, a certain control of temperature in each absorption vessel separately must be made possible. Facilities for this have been insufficient in many cases in the past, and good results have been due more to good luck than foresight.

Suppose now that in a three-vessel system similar to that of Fig. 67 it is required to make 25 per cent. oleum from a gas containing 7 per cent. of trioxide and feed acid of 95 per cent. The production of trioxide is 10 tons *per diem.* It is convenient to begin the calculation with the last absorber, in which the acid must be kept at about 98·5 per cent.

Calculation shows that to produce 25 per cent. oleum from 10 tons of trioxide 15·89 tons of 95 per cent. acid are required. Further, to raise the concentration of the feed acid from 95 to the required 98·5 per cent. H_2SO_4, 2·32 tons of trioxide are required. Since absorption is complete in the third vessel,

[1] *J. Soc. Chem. Ind.*, 1924, 48, 57.

no trioxide leaves it in the gas. If then we equate inlet and outlet for this vessel, we have :—

	Total Tons.	Tons SO_3.	Tons H_2O.
Acid entering 3rd vessel . .	15·89	12·33	3·56
Trioxide entering 3rd vessel . .	2·32	2·32	...
Acid leaving 3rd vessel . . .	18·21	14·65	3·56

The total make of 10 tons of trioxide is conveyed in a gas which contains it to the extent of 7·0 per cent. by volume. Neglecting small changes in total volume due to absorption, the 2·32 tons absorbed in absorber 3 is therefore equivalent to $2{\cdot}32/10\times7$ per cent., or 1·62 per cent. by volume. This percentage is equivalent, as can be seen from Fig. 5, to a vapour pressure of 12·3 mm. of mercury, and this must be the vapour pressure of the acid in the *second* vessel, in accordance with the assumption made initially. The concentration of the acid in the second vessel, its vapour pressure being fixed, will depend on the temperature and, as will appear more clearly when the problem is worked out, we may in this case assume any value that is advisable for the temperature. Let this be 65°. Then, from Fig. 5, it appears that the acid must be 19 per cent. oleum (85·1 per cent. total trioxide) for this is the acid which at 65° exerts a pressure of 12·3 mm.

To convert the 18·21 tons of 98·5 per cent. acid entering the second vessel into 19 per cent. oleum, 5·59 tons of trioxide are required. A total of 23·8 tons of 19 per cent. oleum thus flows from the second vessel to the first. Equating inlet and outlet in the second vessel, we have again :—

	Total Tons.	Tons SO_3.	Tons H_2O.
Acid leaving 2nd vessel .	23·80	20·24	3·56
Trioxide leaving 2nd vessel	2·32	2·32	...
	26·12	22·56	3·56
Acid entering 2nd vessel . .	18·21	14·65	3·56
∴ Trioxide entering 2nd vessel =	7·91	7·91	

This amount of 7·91 tons is equivalent to 5·54 per cent. by volume, or to 42·1 mm. of mercury. By reference to Fig. 5 it is found that 25 per cent. oleum has this vapour pressure

at 70·5°, which must therefore be the temperature of absorption in the first vessel.

By assuming other temperatures for the second vessel any number of solutions of this problem can be obtained. If, however, we are using a two-vessel system, the advantage of which has been pointed out, there is only one temperature for the vessel containing the 25 per cent. oleum, which will satisfy the conditions. The balance which was struck for the third vessel now applies to the second. There are 2·32 tons of trioxide passing from the first absorber to the second, equivalent as before to a partial pressure of 12·3 mm., but in this case this partial pressure is to be equal to the vapour pressure of 25 per cent. oleum, which, as may be seen from the graphs, must therefore be kept at a temperature of 50°. Hence, if the strength of the feed acid and the strength of the oleum to be made are fixed, the temperature in the first (or "oleum") absorber must have a certain fixed value, or the system will become out of balance, and the desired result will be missed. It should be noted that the solution is not affected by varying the temperature in the second (or "98 per cent. acid") absorber, so long as the acid in it is capable of absorbing completely the trioxide passed into it.

It will be found that the weaker the feed acid the higher is the temperature at which the first absorber must be worked. A calculation similar to those already given shows that in the extreme case—when water feed to the second absorber is used, 20 per cent. oleum can be made only if the first vessel is at 75°.

A practical instance is given in the paper quoted, in which the data derived by the method were compared with these observed. In a three-vessel system 20 per cent. oleum (85·27 per cent. trioxide) was being made from 95 per cent. acid (77·66 per cent. trioxide) and a converter gas of 6·7 per cent. Observed and calculated data for the second and third absorbers are given below:—

	Found.			Calculated.		
	2nd Absorber.	3rd	Exit.	2nd Absorber.	3rd	Exit.
Per cent. SO_3 in gas entering	2·18	0·15	0·07	2·76	0·11	Nil
Per cent. total SO_3 in acid	81·2	77·6	...	81·68	77·90	...
Temperature	71·0	63·5	...	...	...	...

Water Feed.—When a plant is required to make either strong acid or oleum without addition of any other acid—in the case, for instance, of a unit producing 98 per cent. acid for the drying towers of the whole plant, it is necessary to work with a water feed. If the process is being carried on, not so much to concentrate acid which is already to hand, as to produce acid directly, a water feed may also be necessary. The water may often be replaced to a greater or less extent by the weak acid produced by the scrubbers and driers of the plant, and in some climates the water obtained in this way may be entirely sufficient. The employment of water or dilute acid gives rise to certain difficulties which are not felt when acid of 85 per cent. or more is used. The weight of acid passing through the absorption system is much less, so that the heating is much more considerable. This effect can be lessened only by applying suitable cooling. There is also a certain difficulty—most appreciable in the case of water—of securing constancy of the comparatively small stream of feed, and to overcome this it has been found advantageous to apply some form of meter to the stream, or to both streams if two are running, one to each section of the absorption plant.

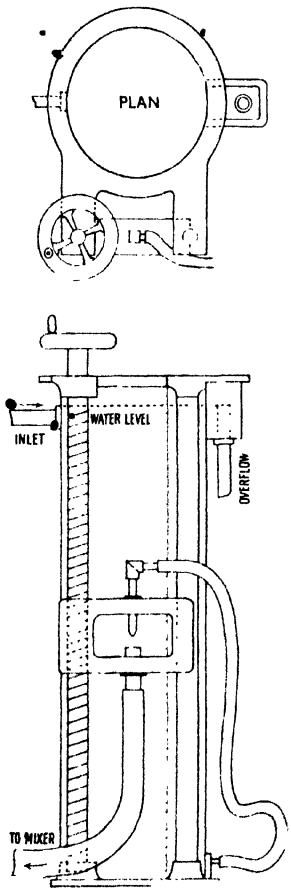


FIG. 71.—Water Meter.

A simple form of meter is shown in Fig. 71. It is made of a piece of 6-in. steel pipe and may be from 2 to 3 ft. high. By means of an overflow, a constant level of water is maintained in the pipe, and the water required is drawn off by means of a rubber tube and carried to a metal jet which is fixed in a block and can be moved up and down in front of a graduated

scale, by a screw. The jet is calibrated by weighing the water run out at several different heads, and a smooth curve drawn through the plotted results. Once set, such a meter works uninterruptedly, and requires no attention, so long as the production of the plant remains the same.

The stream of water is run into the acid just before the entrance to the cooler. If a glass tube is fitted so that the lower end dips well under the moving stream, and a sufficient head is allowed above to prevent the water being blown out by the steam generated momentarily, the dilution gives very little trouble, even with oleum. It is advisable to make the T-piece where the mixing is performed, and the succeeding length of pipe, of some acid-resisting iron, for the mixing is not immediate, and requires a certain length of pipe for completion. This method is also very suitable for the dilution ("breaking down") of oleum.

Making 98 per cent. Acid.—The connections already shown can readily be adopted for this purpose. The two reservoirs are united, and the acid from one of them is thrown up to all three towers. The feed is added before the single cooler, and the general arrangement becomes something like the following.

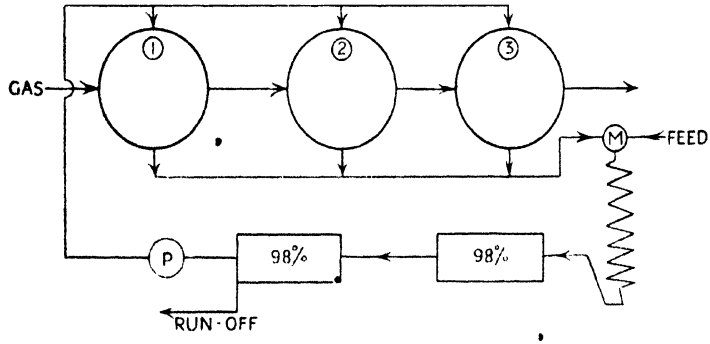


FIG. 72.—Absorption System for making 98 per cent. Acid.

Acid Coolers.—The acid coolers have to remove the heat of reaction, and also any heat which may be given to the acid by the incoming gas. This latter quantity should be small. Many types of acid cooler are in use. In the large plants of H.M. Factories (to which the foregoing remarks are more immediately applicable), the coolers were made in the form of continuous

water-cooled ducts, by arranging 9 ft. lengths of standard pipe with bends, in rectangular blocks. For the oleum sections

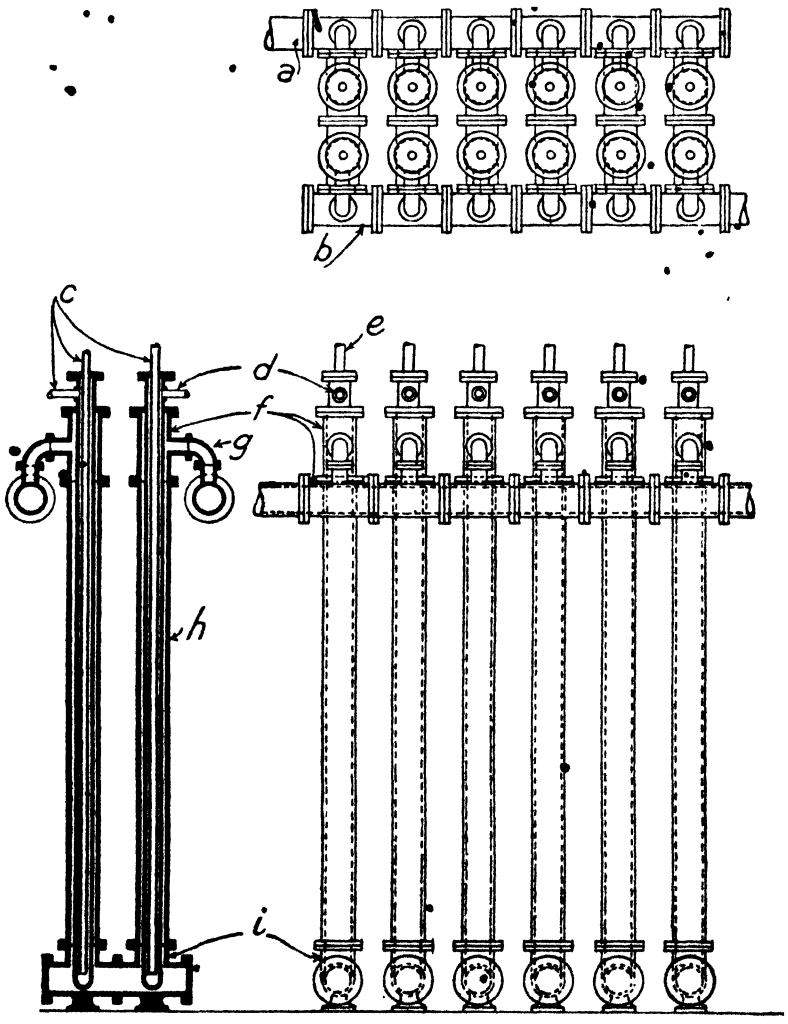


FIG. 73.—Double-Surface Acid Coolers.

5-in. steel pipe was used and for the 98 per cent. acid sections 6-in. cast-iron pipe. In one unit making oleum there were up to 500 linear ft. of steel pipe with a superficial area of 800 sq. ft., and up to 800 linear ft. of cast-iron pipe with an area of about 1650 sq. ft. The absorptive capacity of the unit was from

25 to 30 tons of trioxide per day. With these dimensions the coolers could be relied on to abstract from the acid about 400 C.H.U. per square foot of area per hour. Further details of these coolers will be found in Chapter VIII.

In smaller plants cooling is often carried out simply by jacketing the absorption reservoirs. Double surface pipe-coolers are also in use. Fig. 73 illustrates a set of these. A number are connected in parallel to the acid run-off from the absorption tower. They are built up for the most part of standard steel or cast-iron pipe and fittings. The inlet is shown by *a*, the exit by *b*, *c* is a 1-in. pipe carrying the water to the bottom of the internal cooling pipe, *g* is a standard 2-in. bend, and *f* and *i* are standard 6-in. T-pieces.[1] Coolers have also been made in the form shown in Fig. 74.

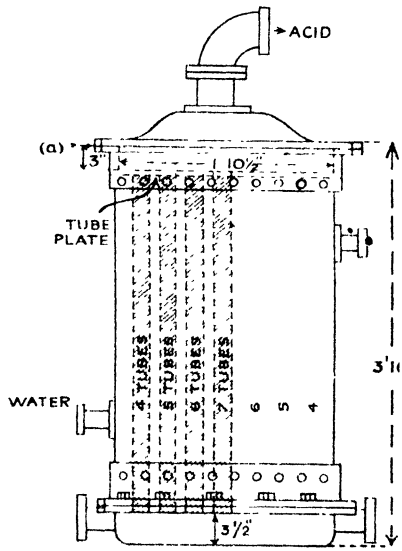


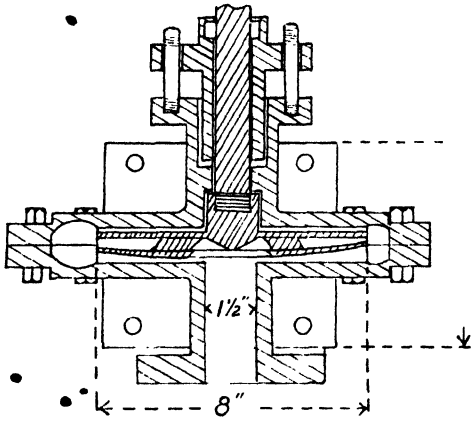
FIG. 74.—Acid Cooler.

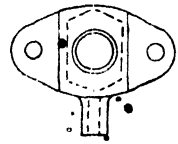
Pumps for Circulation and Transfer of Acid. — Oleum and concentrated acid are often circulated between the tanks and absorption towers by cast-iron centrifugal pumps, coupled directly to motors on the same base-plate. The pumps can be of quite simple design. An example is shown in Fig. 75 which, coupled to a 4 h.p. motor, and running at 1400 to 1500 r.p.m. will elevate each hour about 12 tons of 20 per cent. oleum to a height of 40 ft. The impeller is 8 in. in diameter. The gland is made in the form shown on the right, with a hollow box and a short bent pipe pointing downwards, by which any leakage may be led away to drain. A jet of water is sometimes directed on to the top of this gland-box. Another design is that of the Rees-Roturbo pump shown in Fig. 76.

The principal point of trouble with these pumps is the packing. Good results are obtained by using white asbestos

[1] *U.S. Dept. of Int., Bull.*, 1920, **184**, 188.

cord which has been heated in mineral jelly for twenty-four hours. A mixture of nearly the same composition as the "rubber-grease" of the laboratory and consisting of raw crêpe rubber, vaseline, and paraffin wax, heated and well mixed, has been used very successfully to impregnate blue asbestos cord for the same purpose. Nevertheless the packing of circulation pumps in an absorption house is always liable to cause loss of time and interruption of working.





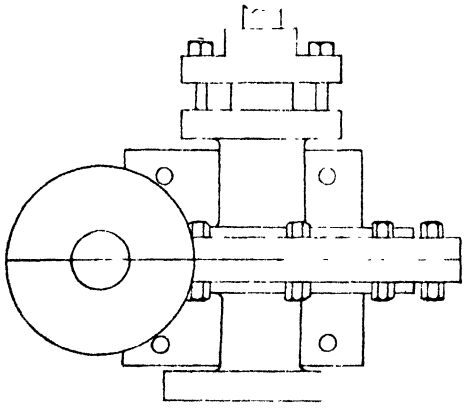


FIG. 75.—8 in. C.I. Centrifugal Acid Pump

To overcome this difficulty several modifications have been tried. One device, apparently not used to any considerable extent, is to divide the stream of acid entering the pump into two, one on each side of the impeller; both sides of the impeller, and consequently the gland, are then under suction when the pump is working. So far as pumps attached to circulation tanks are concerned, it is far the best to dispense with the gland altogether.

This is done in the design of Fig. 77, which represents the pump used in the absorption houses of the D.E.S. Grillo plants.

The delivery is 2 in., the impeller 10 in. wide. The suction is on the under-side, and in the actual suction-inlet is a bearing for the shaft which runs inside the vertical hollow cast-iron pillar. This pillar is prolonged above the level of the acid in the tank, so that there is no outlet except through the delivery pipe, and no gland to pack. The bracket bolted to the head of the pillar carries a thrust-bearing and below this a ball-bearing. The drive is from a motor through a quarter-twist belt. These pumps were capable of throwing about 25 tons of acid per hour to a height of 30 ft., and were very regular in running.

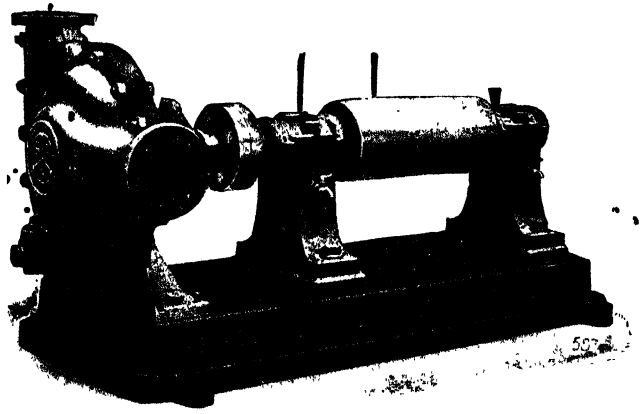
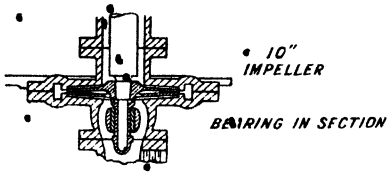


FIG. 76.

A similar pump, of somewhat different design, is made by the Rees-Roturbo Company, and is shown in Fig. 78.

Cooling the Gas before Absorption.—The first stage of this operation is usually carried out as a process of regeneration, by which the gas entering the converter undergoes part or all of its heating. In this way the temperature of the converted gas is reduced to say, from 200° or 250°. The remaining heat is abstracted as far as is necessary by passage through coolers built up of pipe sections. The Mannheim plant is an exception, for here a cylindrical steel cylinder is in use. Such pipe sections are usually cooled by air-circulation. With a heavy load the assistance of water may be necessary, but it is found that the sudden fall of temperature due to running cold water is apt to cause some change to occur in the gas, so that absorption becomes imperfect and



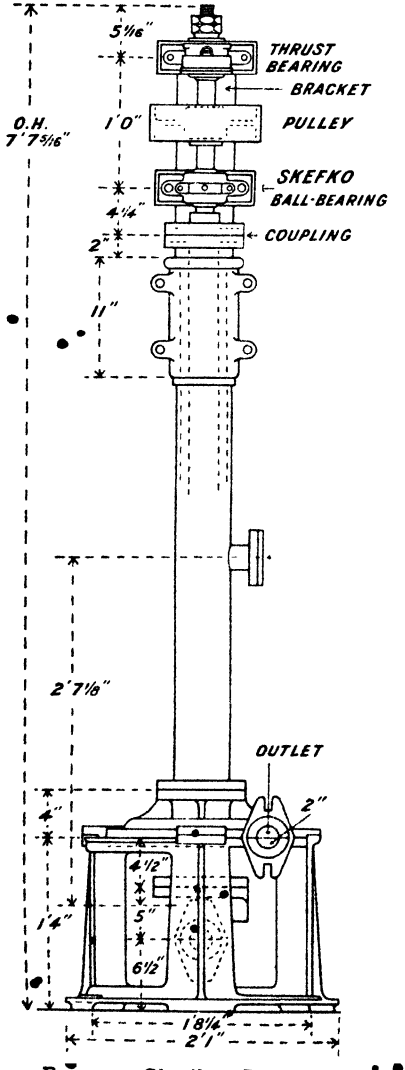


FIG. 77.—Glandless Centrifugal Pump.

unabsorbed mist passes away from the absorption towers, which before the change were working normally. It is therefore advisable to use a water-

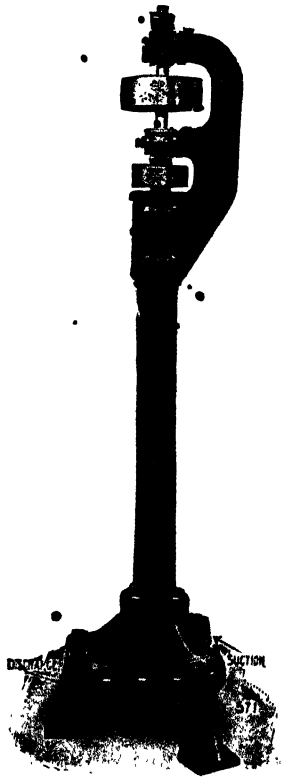


FIG. 78.—Glandless Centrifugal Pump.

spray if water is to be applied at all.

The temperature at which the gas leaves the cooler and enters the absorber is important in its

relation to the whole process of absorption. From 50° to 70° is generally preferred, and the temperature might even exceed this somewhat without harm being done, if it were not that the resulting hot circulating acid becomes rapidly less capable of absorption as the temperature rises, and much more corrosive. Care is always taken not to go below the lower limit, for at 30° or even higher, condensation of solid material is apt to occur in the pipes and block them up. This trouble may readily arise on a plant which runs on a varying load. One day the cooler is hardly large enough; on another it is too cold and may even have to be warmed.

The cooler may consist of batteries of 6-in. steel pipes set horizontally, as in the Ministry plants, or of a bundle of pipes set vertically, and connected to the tube plates of two short headers, as in the Tentelew and other plants. For a plant producing about 12 tons of trioxide per day, there may be from fifty to sixty 2-in. steel tubes each about 12 ft. long. A very similar construction adapted to the Mannheim Process, with the addition of a larger bottom header to allow of a cleaning door, is shown in the gas-cooler of Fig. 79. The headers of tubular coolers are sometimes extended to form an envelope enclosing the bundle of pipes, the acid gas then passing round the pipes instead of inside them. This allows air to be drawn through by means of a chimney, and the cooling effect made more or less intense at will (see Fig. 34). Another type of cooler used on the

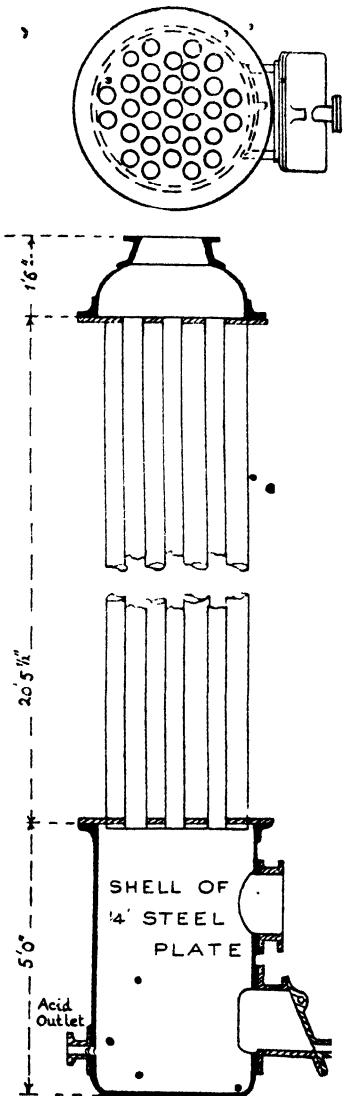


FIG. 79.—Converter-Gas Cooler.
(Tubes, 4-in. bore; 5½-in. pitch.)

Mannheim plant for cooling not only the converter-gas but the burner-gas also, is shown in Fig. 80. It consists of a simple cylindrical steel shell standing on a cast-iron saucer. Four baffle-discs are fixed in the shell at equal intervals apart, so that the gas passing upwards is thrown against the wall, down the outside of which water trickles from the serrated edge of the cup sunk in the top.

Another method of cooling the converter-gas and utilising at the same time some of the heat carried by it, has been put

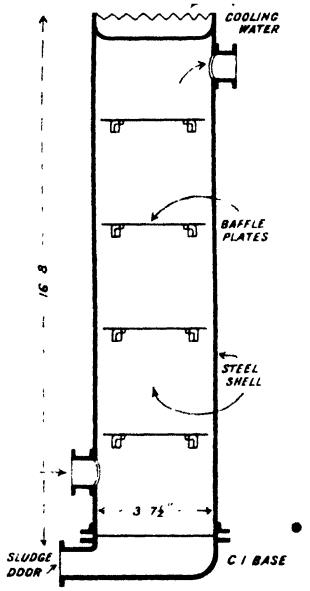


FIG. 80.

in operation (British Dyestuffs Corporation and Davidson, B. P. 132923 of 1918). The hot gas is passed round the coils of a heat-exchanger through which oleum of 20 to 40 per cent. is run. The sulphur trioxide vapour which is given off is passed into an expansion chamber and then into a jacketed absorber containing oleum of the same strength as that mentioned (the product of the absorption system of the plant). In this way a concentration of 80 per cent. of free trioxide can be reached. The acid flowing from the coils can be used in the plant as feed.

CHAPTER VIII

GRILLO PLANTS

THE Grillo methods of sulphuric acid manufacture had their origin, as has already been related in Chapter I., in the endeavours of Schröder and the *Aktiengesellschaft für Zinkindustrie, vormals W. Grillo*, first of all to utilise liquid sulphur dioxide made by the process of Hänisch and Schröder and later (after 1897), to treat the gas from the zinc-roasting furnaces directly. It is interesting to recall that at this date the experiments of the larger firms must have been nearing completion, if they had not actually reached it.

The patents taken out by Schröder and Grillo have been referred to in the appropriate places. The one distinguishing feature of the system is the use of magnesium sulphate as catalyst-carrier. The methods of purifying the burner-gas involve no operation of outstanding efficacy, their main feature being intensive filtration through fine coke. Scrubbing with sulphuric acid is carried out in packed towers designed for this purpose, or for drying in addition. Thorough washing with water or alkaline solution is not used. For these reasons the purification of gas from pyrites-burners has been, in most plants on the Grillo system, an imperfect one, and in some has failed altogether. That this would be necessarily the case appears to have been recognised by the inventors, who laid special stress on the ease with which the contact-mass could be reworked when it had become too inactive to be kept in use. So far as the use of pyrites or other sulphide ore is concerned, plants embodying these ideas have represented a compromise which in the most modern practice no longer finds favour. Renewal of the large amounts of mass contained in a full-sized unit is at the best an expensive operation, apart from the inevitable loss of platinum, the cost of which has increased enormously

since the method first came into use. Many plants are in operation, however, in which pyrites is burnt, the contact-mass being renewed more or less frequently.

But if sulphur is to be used the purification required is in general much less rigorous, and the Grillo system becomes a thoroughly practicable one. The comparatively simple design of the plant lends itself readily to the construction of large units which can be economically run, and with the complete combustion always obtained with sulphur, the efficiency can be high. Such plants may therefore be of great use in circumstances in which sulphur is cheaper than ore, or very rapid construction is more important than a certain loss in operating cost. For this reason they were largely relied on for war-time production.

To adapt the system for burning pyrites, and even in some cases for sulphur, many changes have been made. Glover towers have been built to scrub the hot gases, and the Tentelew methods of purification have been adopted either wholly or in part. It is probable, in fact, that the increasing efficiency required of any type of pyrites-burning plant that is to hold its own will, before long, efface any distinction that there may be, other than the use of sulphate of magnesia, between the Grillo and other types of plant. It is also possible that Grillo contact-mass may be employed in other systems which, before the expiry of the Grillo patents, were confined to asbestos as a carrier.

The following list of the Grillo patents was communicated to Lunge in 1911 by the Company (last edition of this work). The British patents have all expired, and the more important of the American patents ran out in 1918. It is stated that the General Chemical Company of New York, which came into possession of the rights as the result of litigation with the New Jersey Zinc Company (the first holders), had the right to issue licences to erect and run such plants, until 1923.[1]

(1) *Contact Substances.*—Ger. P. 102244; Fr. P. 283496; Belg. P. 140984; Aus. P. 565; Hung. P. 15502; It. P. 54742; Sp. P. 25637.

[1] *U.S. Dept. of Int., Bull.*, 1920, 184, 152

(2) *Recovering Sulphuric Acid.*—B. P. 25158 of 1898; Nat. P. 23 of 1901; Cape Col. P. 1280.
(3) *Contact Furnaces.*—B. P. 17034 of 1900; Ger. P. 138695; Fr. P. 304530; Belg. P. 152713; Nat. P. 157 of 1901; Cape Col. P. 1445; It. P. 57464; Sp. P. 26728; Switz. P. 22762.
(4) *Catalytic Apparatus.*—Aus. P. 12287; Russ. Ps. 8372, 8373, 8446.
(5) *Purification of Contact-mass.*—Ger. P. 115333.
(6) *Preparing Contact-mass.*—B. P. 10412 of 1901; Ger. P. 128554; Fr. P. 311689; Belg. P. 156974; Nat. P. 156 of 1901; Cape Col. P. 1446.

The Grillo Plants of the D.E.S.

The Grillo plants which were erected as integral parts of several of H.M. Explosives Factories were designed by K. B. Quinan and his staff of the Department of Explosives Supply. As emergency installations, and in order to act as supplementary producers of acid, numerous Mannheim units were first put up, but the greater part of the oleum used during the War was made in the batteries of Grillo plants at Queen's Ferry, Avonmouth, and Gretna. The production of sulphur trioxide at Queen's Ferry alone was at one time 250 tons per day.

When erection was undertaken, the question of freights had already become important, and sulphur was preferable to pyrites from this point of view. The greater efficiency obtainable, and the simplicity of burning sulphur completely with unskilled labour, were considerations which bore in the same direction. Work on these plants was begun about the end of 1915, and the first unit was started at Queen's Ferry in July 1916. Other units were put in operation in rapid succession at all three factories. A single unit was also built at East Greenwich, in the chemical works of the South Metropolitan Gas Company, and was run in connection with the large synthetic phenol plant built and operated by them. There were eventually ten units at Queen's Ferry, four at Gretna, and twelve at Avonmouth.

The rating of each unit was nominally 20 tons of SO_3 in

twenty-four hours, but the make could actually be raised to 25 tons, or even more, at the cost of a slight loss in efficiency. The units were built in pairs, each pair being symmetrical about the line running the length of the plant from sulphur burners to absorption-house, so that a "left-hand" and a "right-hand" unit faced each other in each building. The burner-house, converter-house, and absorption-house were spaced out with plenty of room between each other and the corresponding houses of other units, and were built of steel, with roofs and walls of corrugated sheeting. It should be emphasised that although two units were placed in the same buildings they were quite independent of each other.

Shortly after the Armistice all these plants were shut down and some of them have already been dismantled. As is well known, it is proposed to use the Avonmouth plant in connection with the roasting of zinc ores on a very large scale and Delplace burners were installed. It may be questioned whether the purification arrangements will prove equal to the work, in view of the difficulties which are known to arise from the impurities generated from zinc blende, unless considerable modifications are made in the design.

The question has often been asked: Whether the sulphur burners of these plants could be replaced by pyrites-kilns. Sufficient data will be given to show that the purification was generally less perfect than such a transition would demand, and in the opinion of many who are competent to judge, the structural changes required would have been considerable.

From the time that they were put in operation until, in some cases, after the Armistice, experimental work was almost constantly in progress on these installations, and much experience in their regulation was acquired by a large number of persons. It should not be thought, because so many are now unused or dismantled, that the experience gained with them has been no general value. To some extent these units were modelled upon those of the Cape Explosives Company. The Grillo type is not the most modern and scientific, but it is very widely used, and numerous systems are in action all over the world, compared with which the now derelict plants of H.M. Factories are improvements and enlargements. They were designed with great forethought and liberality,

and their erection as permanent structures left little to be desired.

The account given below of the construction of these plants owes much to that published in *Technical Records of Explosives Supply* (1921, No. 5). From this source the larger drawings have been reproduced. The matter of the second section below, dealing with operation, was drawn mainly from personal experience.

The Function of the Plant in the Acids System.—The Grillo plants in the factories producing nitro-cotton and nitro-glycerine for cordite, or making T.N.T., served, like nearly all oleum plants in explosives works, the double function of producers and concentrators of sulphuric acid. There were, in addition, Gaillard or other types of concentrating apparatus, but no other producing plant. In full operation of a whole system, the contact-plant was arranged to supply just so much fresh acid as was required to replace the losses in manufacture and no more. The one large loss is that of sulphuric acid at the retorts producing nitric acid.

The cycle of operations in which the contact-plant is involved may be well illustrated by the manufacture of R.D.B. cordite[1] at Gretna, for which a part of the flow sheet, with quantities relating to 100 tons of cordite, is produced in Fig. 81. For the production of acid for nitrating glycerine, 20 per cent. oleum from the Grillo, and strong nitric acid were mixed; for nitro-cotton acid concentrated sulphuric acid was used in addition. The nitro-glycerine spent acid was deprived of its nitric contents in denitrating towers, and returned to the Gaillard towers, thus furnishing feed for the Grillo plant. The nitro-cotton spent acid was partly resolved into its constituents in the same way, but by distillation, and was partly strengthened again for use by addition of a revivifying mixture in making which both oleum or concentrated acid might be used. All sulphuric acid, therefore, returned again to the concentrators and some of it to the contact-plant, excepting that which was lost in nitric acid manufacture, and was equal to the production of the contact-plant when the amount in circulation or storage remained constant.

[1] Cordite made from nitro-cotton gelatinised with alcohol-ether instead of acetone.

The production of fresh acid by the contact-plant being limited, its capacity for concentration is limited also. Reckoning in terms of H_2SO_4 and H_2O (oleum then having a minus quantity of water), it can be seen from the flow sheet that of 86 tons of water returning to the Gaillards (omitting 4 tons which come

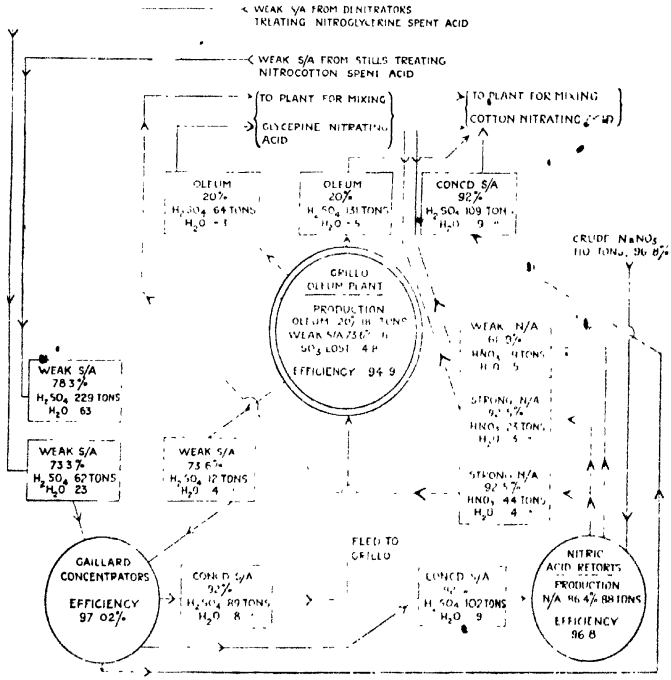


FIG. 81.—Acid Flow-Sheet for R.D.B. Cordite Manufacture.

from the Grillo as weak acid, and may be considered to be in circulation between the two), only 12 are eliminated in the contact-plant.

1. Construction and Arrangement.

The general arrangement of a single unit can be viewed in the plan of Fig. 82 which, for the main part, is drawn to scale, and shows the whole course of the gas. The principal elements of the unit may be indicated as follows, in order:—

Sulphur Burners and Dust Chamber ("heater-cooler").

C. CONVERTER
H. HEAT-EXCHANGER
H.C. HEATER-COOLER
P. PRE-HEATER
F. PRE-HEATER FIRE-BOX
V. VALVE

C. ACID COOLERS
A. ABSORPTION TANKS
T. ABSORPTION TOWERS
W. WEIGH TANK
S. STOCK TANK FOR OLEUM
p. PUMP

H·M· FACTORY GRETNA.

GRILLO OLEUM PLANT.

DIAGRAMMATIC PLAN.
OF ONE UNIT (HALF-SECTION)

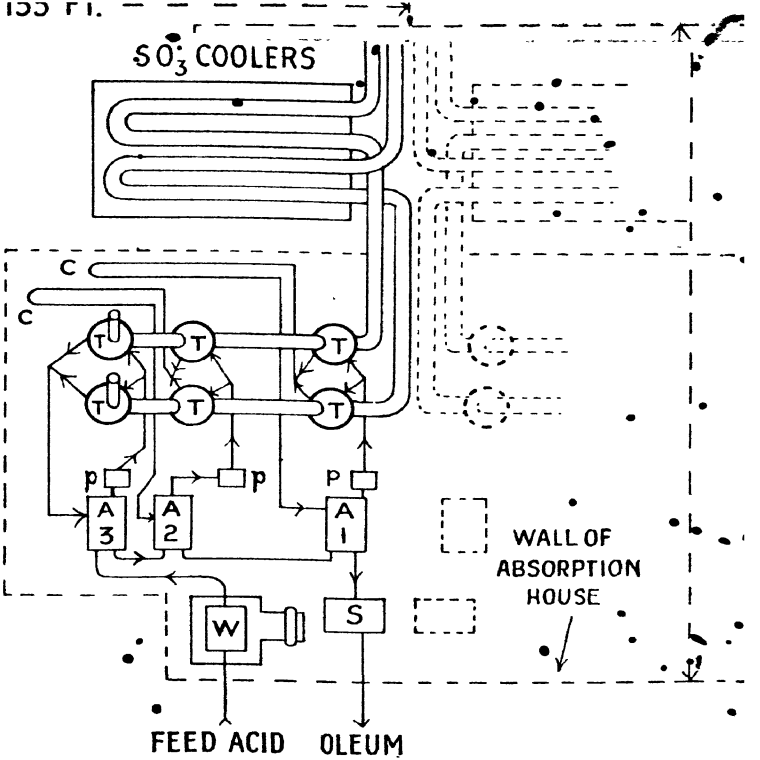


FIG. 82.

[Face page 294.

Purification System—Burner-gas cooler ("SO_2 cooler"), first two filters, scrubbing and drying towers, final three filters. *Conversion and Regeneration System*—Blower, grease-catcher, heat exchangers, "heater-cooler," preheater, converter, converter-gas cooler ("SO_3 cooler"). *Absorption System*—Towers. From the plan it will be observed that shortly after the purified gas left the blower of any unit it divided into two streams, which then followed similar but, for the most part, separate channels. There were therefore two converters, two in each unit, and four to each converter-house.

Sulphur Burners and Dust Chamber.—In each unit there were twelve sulphur burners of the pan type set in a row. They were built of brick braced with channel irons and tie-bars carried through the brickwork in steel pipes. Their construction may be seen from the sketches of Figs. 83 and 84.

The cast-iron pans (P), into which sulphur was charged by hand once an hour, were 7 ft. 2 in. long, 3 ft. 6 in. wide, and 5 in. deep. The opening to the pan was formed by an iron casing which was fitted on the outside with a sliding cast-iron door (D_1), in which were a number of slots capable of being closed by means of a slide. Entering through one or more of these slots, the air caused the sulphur partly to burn, and partly to boil, and the resulting gas and vapour were drawn up from the pan at the back of the first arch. At this point "secondary" air was admitted from the cooling-flue F, which ran the whole length of the block of burners, by means of the port and slide (p_1). Finding its way through the sixteen small ports in the upper arch, the gas then entered the block of chequer-work brick which was built up on this arch, and by passage through it became thoroughly mixed, combustion being assisted by additional air drawn in through p_2, and occasionally through p_3 and p_4. The apparent complication of these arrangements is due to the need of burning the sulphur steadily. If all the necessary air were drawn into the pan at the front, most of the sulphur would boil away outright, and there would be great "sublimation" of a fine mist of sulphur into the purifying. The thorough mixing in the red-hot chequer-work is important safeguard against this.

Space G_1 above the chequer-work extended without through all burners alike, and, at the end of the

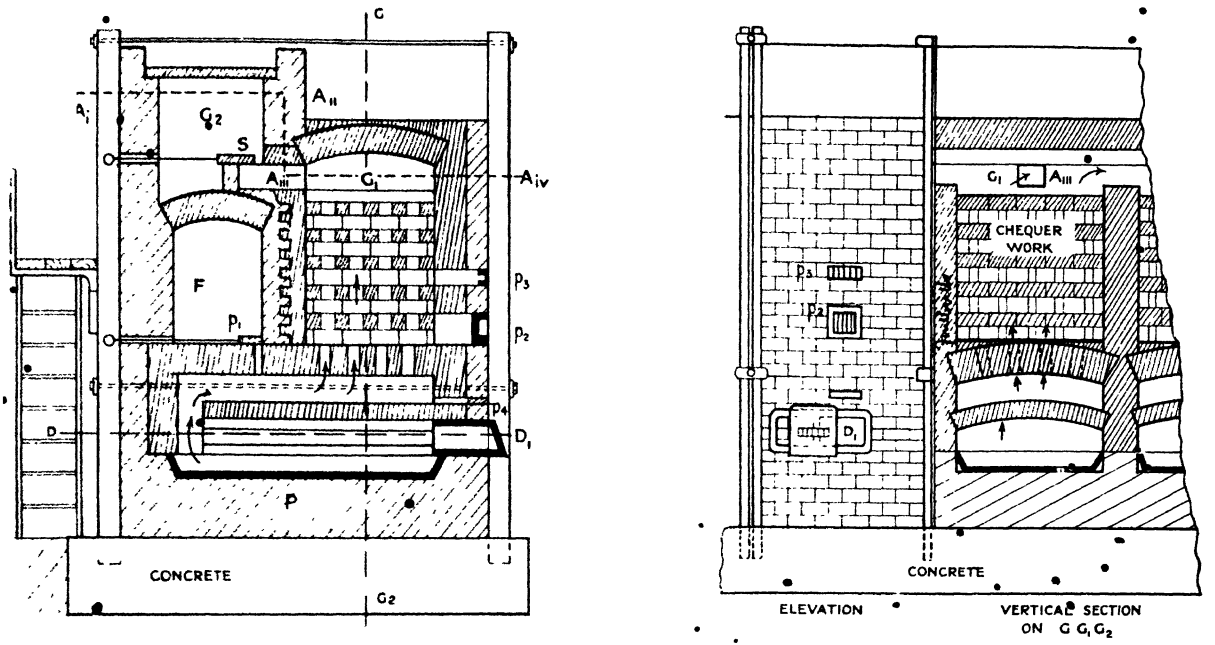


FIG. 83.—Grillo Sulphur Burners—Vertical Sections.

block remote from the rest of the plant, this burner flue G_1 ran into the main flue G_2 by which the gas was led away. But this arrangement by itself would have produced an inequality of draught from one kiln to another, and to prevent this a short-circuit slide S was provided above each burner through which gas could escape directly into the main flue. It is easy to see that, with equal draught on each kiln, the opening of the slides (S) will have to be increased towards the end of

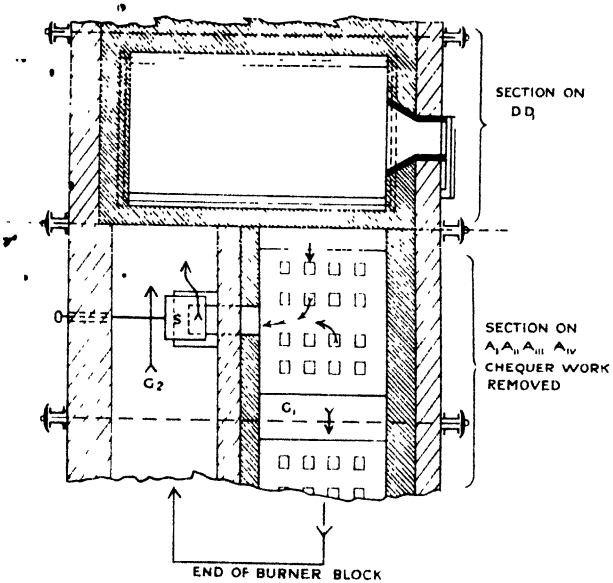


FIG. 84.—Grillo Sulphur Burners—Horizontal Section.

the block where the two flues join. The regulation of these slides is an important point. The main flue G_2 was covered with tiles, and the channel filled with sand or other insulating material, and it was found advantageous to increase the general temperature by affixing more or less lagging, particularly in windy situations. The weight of a block of twelve burners was about 340 tons.

Arriving at the end of the main flue G_2, the hot gas passed downwards into the "heater-cooler" by a downtake of the flue. At the foot of this downtake, as may be seen from the plan of Fig. 82, was a 15-in. cast-iron connection to a chimney flue, by means of which the burners could be connected to the

chimney on removing a damper. This was necessary when starting up, or sometimes during running, when the plant had temporarily to close down. The bottom of the downtake was connected by means of two short brick flues to the "heater-cooler"—a brick chamber about 23 ft. 6 in. long, and 16 ft. wide. This will be detailed in connection with the regenerative system of the plant. It was divided longitudinally by a central wall (Fig. 90), and three low walls about 18 in. high were built across the floor at right angles to the gas-stream in order to retain the dust, which, when it had accumulated, could be cleaned out through arches at the end of these walls. The floor of the chamber was given a slope towards these arches from the central line. In the two chambers were hung the cast-iron pipes through which the purified gas passed immediately before entering the converter. By passing over them the burner-gas was cooled, but was always hot enough to prevent any condensation of acid on the brickwork.

Purification System. — At the other end of the "heater-cooler," the gas passed on through two brick uptakes, on which were seated the bases of two steel pipes which led to the "SO_2 cooler." These connections, and the general appearance of the cooler, are shown in Fig. 85. There were two similar systems, each comprising twenty lead pipes, 20 in. in diameter, and made of 20 lb. lead. The steel pipes were connected to the first two lead pipes by means of spigot and faucet joints, filled with asbestos packing, in order that the expansion and contraction of the steel pipes should not pull the lead out of shape. The bottom headers of all the pipes were submerged in water in a wooden tank, and a leaden water supply pipe was arranged to spray water round each pipe just below the flange which closed the top. It is important that a reliable source of water be available, for if it fails, the first pipes of such a series are very liable to buckle rapidly with the heat of the hot gas entering them. The water ran down the outsides of the pipes into the tank, and from this to the drain. The bottom headers projected beyond the sides of the tank so that the flanges on the headers could be removed, and the inside cleaned out with a hose. This operation was facilitated by the provision of a sloping launder just under the flanges. Permanent tie-rods bore the weight of the flanges from the upper part of

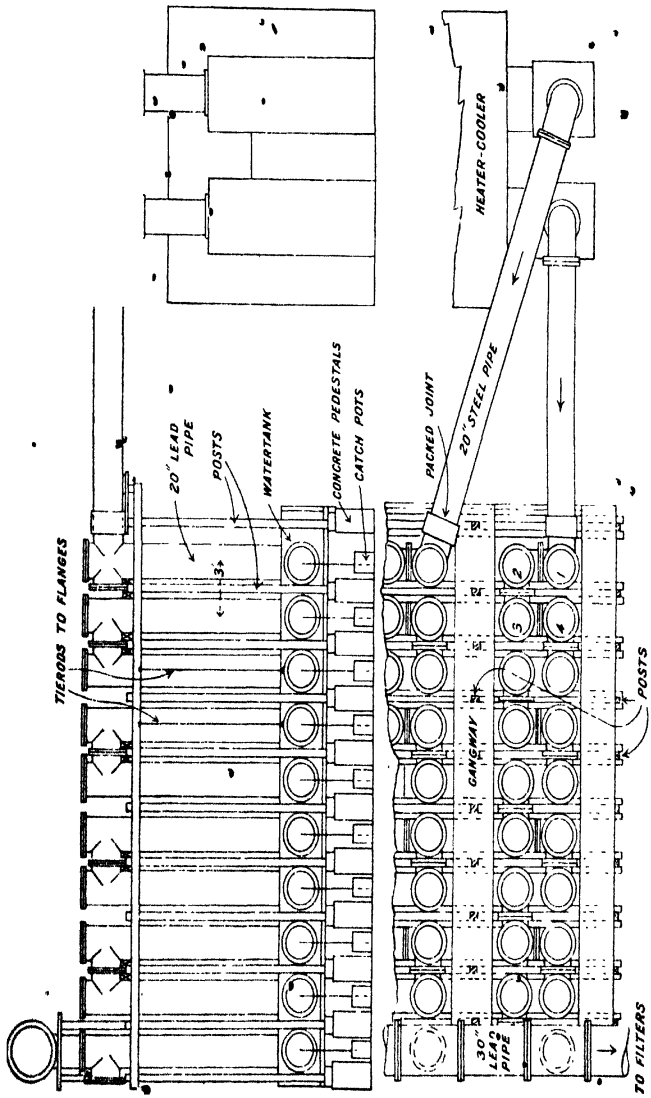


FIG. 85.—Burner-Gas Cooler.

the wooden structure of the cooler, and could be used to swing the flanges aside when they were unbolted.

To each bottom header was provided a drain pipe which was luted into a leaden catchpot standing below. Into these pots the acid ran which condensed in the cooler, and overflowed from them into a pipe common to all. This pipe delivered to a sump from which an air-lift raised the acid into a launder serving also for the weak acid from the filters and scrubbing towers.

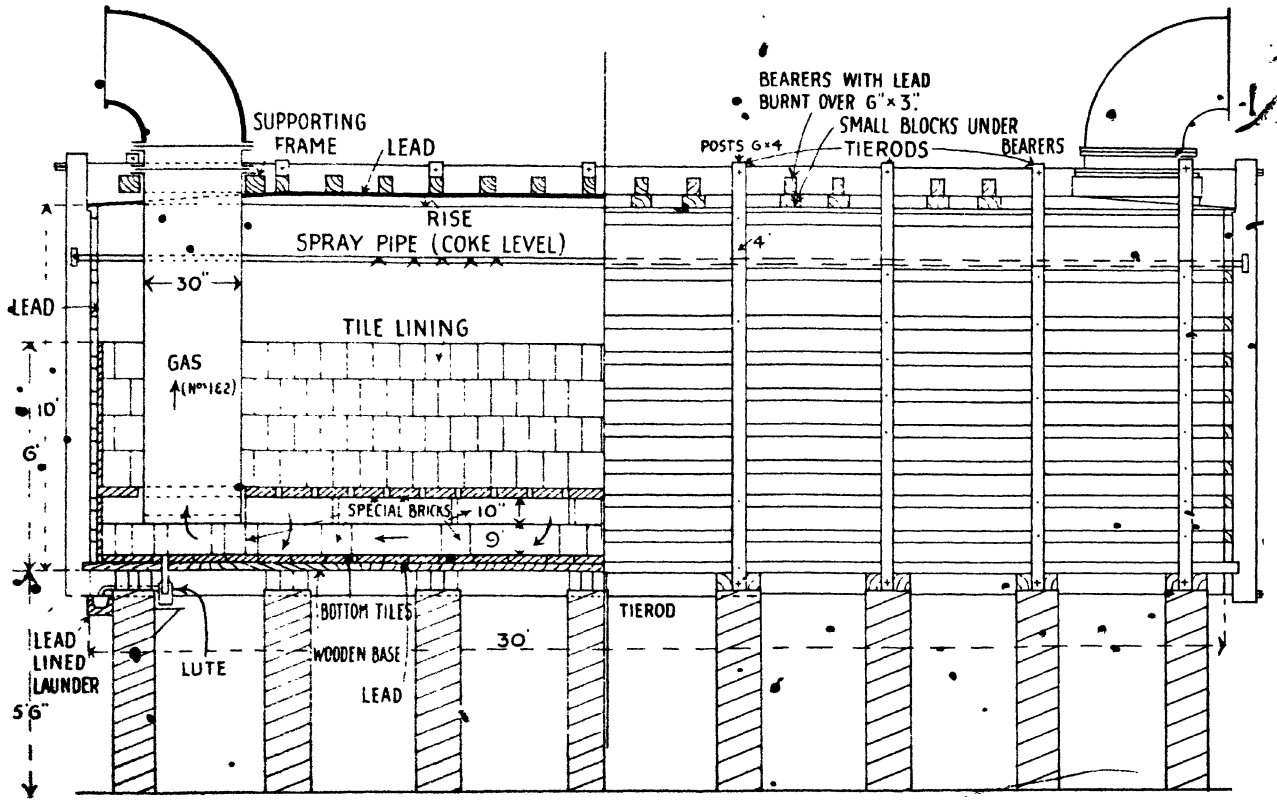
The gas entering the first header, No. 1, passed downwards and through the short water-cooled branch into No. 2 (Fig. 85, plan). Rising upwards in No. 2 it crossed to No. 3 by the upper header, down again and across to No. 4 by a lower one, and so on. The streams from the two halves of the cooler were delivered at the end into a 30-in. lead main which was connected to the first filter. The temperature in this main was in general only slightly above atmospheric. This cooler was of liberal dimensions and was even more than sufficient to cool the gas from 300° or so, when maximum charges were being burnt. The only possibilities of trouble were, first, that the cooling of the first pipes might be interrupted, and second, the corrosion of the connecting steel pipes. These are always liable to be corroded, in spite of their being lined with acid-proof material as was usually done, and in at least one factory they were remodelled entirely. In this case the uptakes from the "heater-cooler" were brought round to face the cooler and built up to such a height that the connection could be made with very short lengths of cast-iron pipe. This proved satisfactory.

There were in all five filters placed side by side on brick kilns and filled with coke. After leaving the "SO_2 cooler" the gas passed through two of these in succession, in each taking a downward direction through the coke. The main reason for this downward passage is that any dust, or finely divided "sublimed" sulphur from the burners is deposited on the top of the coke, and if the filter is choked up in this way it can be freed by opening up and removing the upper layer of packing, or in many cases, by simply raking over the top. Finely divided condensed sulphur, however, is very difficult to remove, and was occasionally known to pass right through both filters.

All five filters were built and packed in the same way, the

only difference between the two first and the last three being in the direction of flow. A section of one of them is shown in Fig. 86. It consisted of a box of 8 lb. lead, about 30 ft. long, 12 ft. broad, and 10 ft. high, constructed in a solid wooden framework, the lead being burnt round the bearers at numerous points to keep it in place, particularly at the top, to resist the suction which tends to make it fall in. The bottom of the filter and the sides, to a height of 6 ft., were lined with acid-proof tiles, and the bottom was laid with acid-proof bricks. On this bottom, with similar bricks and some special tiles, was built up a grid on which the coke was piled. The gas entering by the 30 ft. lead pipe was led into the free space above the coke and, passing downwards, found its way through the grid into the free space below, which extended the whole length of the filter. From here it escaped by the other 30-in. pipe, the end of which, reinforced with a steel band, rested on some special bricks. The acid condensing in the coke was collected at one end by reason of the difference in height of $\frac{3}{4}$ in. between the ends of the filter, and was delivered into a luted catchpot, and then to the launder already mentioned. Each filter was fitted with two leaden spraying pipes which ran along the surface of the coke for its whole length; by means of these, acid could be run into the coke. This was a useful facility when the filters froze in cold weather, as occasionally happened. There was also a sight-glass in the form of a bell-jar, luted into the top, through which the clearness of the gas could be inspected. On some plants glass windows were provided opposite each other in the ends so that a column of gas 30 ft. long could be looked through at will.

These two filters assisted the rest of the purification system very considerably by removing a large proportion of acid mist (*i.e.*, both water and sulphuric acid) before the scrubbers were reached. The specification of the packing was as follows: At the bottom, 24 in. of coke 4 in. to 6 in., then 12 in. of 4 in., 12 in. of 2 in., 4 in. of 1 in., and 48 in. of $\frac{1}{8}$ to $\frac{3}{16}$ in.—total weight of coke in one filter about 45 tons. Unfortunately, this specification was not always regarded with strictness, with the result that some plants were not so efficient in regard to both the preliminary separation of mist in Nos. 1 and 2, and the final one in Nos. 3, 4, and 5.



GRILLO PANELS

FIG. 86.—Coke-filled Gas Filter.

Leaving the second filter, the gas passed into the bottom of the first scrubbing tower, and from the top of this into the bottom of the second, and similarly through a third. A plan and elevation of this battery of towers is seen in Figs. 87 (2) and (3), and also a vertical section of a single one in (1). Although circular towers were erected at Avonmouth the usual type was square. The lead casing had sides about 12 ft. wide, the lead being burned to cross-beams depending from the four principals of the tower at numerous points. It extended to within 3 in. of the base in which the tower stood, the lower end being left free to allow the acid to escape, and to take up any "creep." On the lead tray was laid a $4\frac{1}{2}$ acid-proof brickwork lining, which was continued up the sides of the tower to within a few inches of the gas-outlet pipe at the top. At the base, on each side of the inlet, open brickwork walls were built on the base lining to a height of 3 ft. 9 in., and on these walls and the brick chequer-work at each side of them a grid was built up by acid-resisting tiles 30 in. × 10 in. × 4 in., laid on edge. The entering gas passed into the central channel and from it to the chequer brickwork, and was therefore distributed evenly before passing upwards. The coke packing consisted mainly of selected pieces from 6 in. to 8 in., with which were worked in smaller pieces not less than 4 in. in diameter. Short branches (30 in.) closed with flanges were fitted at top and bottom for inspection.

On the top of these towers was arranged a distributor-room, and above this a tank-room (Fig. 87 (2)). The acid thrown up to the tank room from the ground level was blown into a splash-box in the particular feed-tank concerned. From there it flowed downwards to the distributor on the floor below. The acid for each tower was split into seventy-two streams in two distributing trays, and was run to the lutes in the tower top through the same number of narrow lead pipes. These lutes were fixed in a lead-covered steel plate which formed the cover of the tower proper. The level of the coke was some 4 ft. below, and the drains of the lutes near the gas-outlet were prolonged almost to this level, so that the risk of acid being blown into the outlet as it fell was avoided.

Having percolated through the coke, the acid ran off from the saucer of the tower into a lead cooler made with coils for water circulation, and then into the low level feed-tank

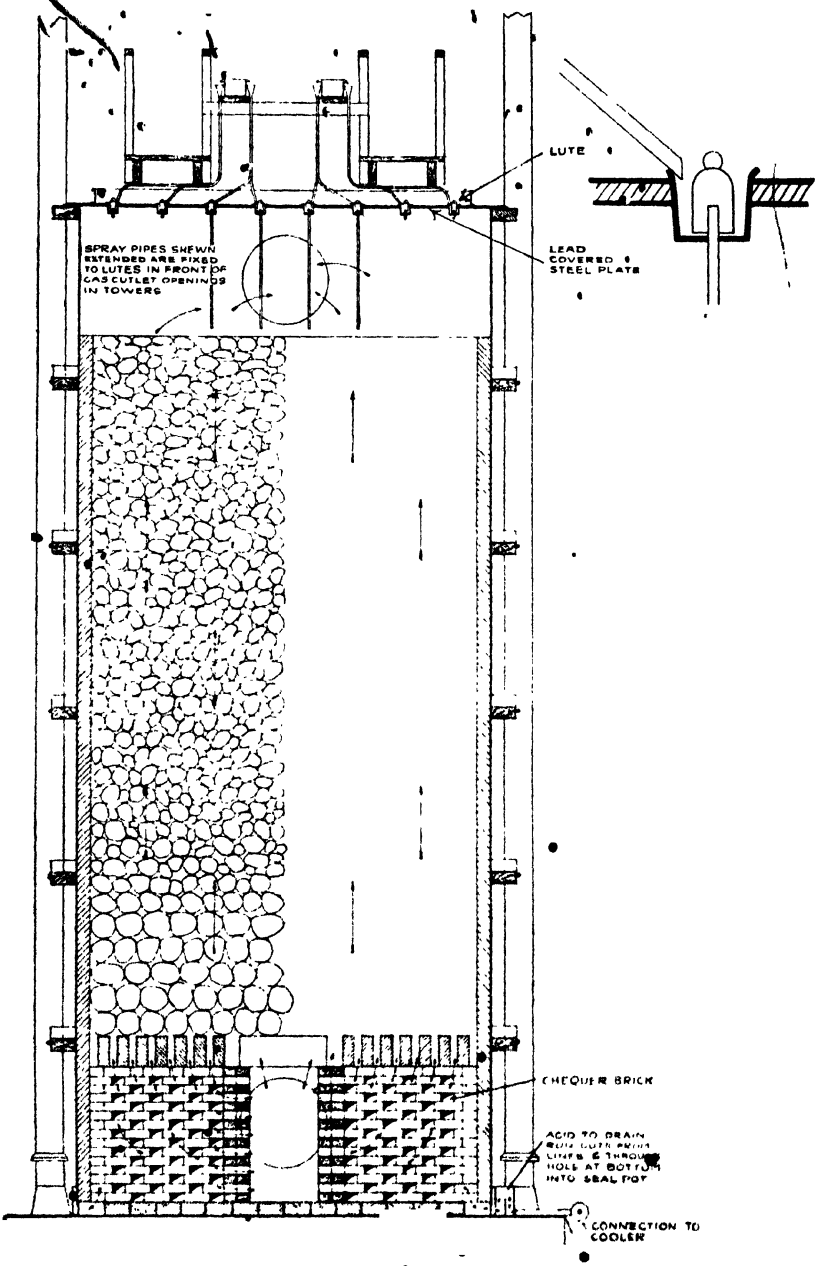


FIG. 87 (1).—Grillo Scrubbing Tower (Sectional Elevation).

FIG. 87 (3).—Grillo Scrubbers (Plan).

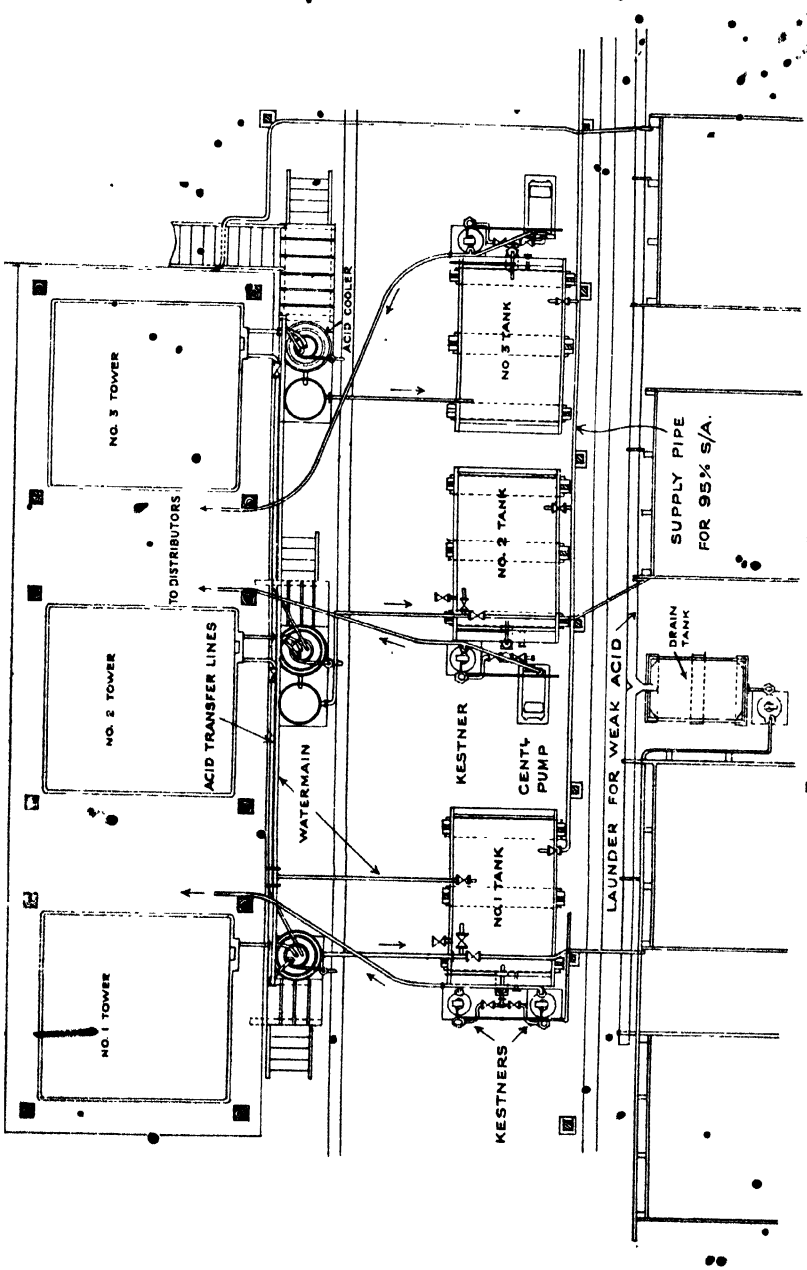


FIG. 87 (3).—Grillo Scrubbers (Plan).

in front of the tower (another outlet besides that through the cooler was in fact necessary for heavy feeds) (Fig. 87 (2) and (3)). Pipes were also fitted through which acid could be transferred from the saucer of No. 3 or No. 2 tower (using the numbers for the order of the *gas* transference) to No. 2 or No. 1. Circulation round No. 3 and No. 2 was maintained in each case by a 10-in. centrifugal pump. For No. 1 scrubber, in which, on occasion the acid might be reduced in strength to 60 per cent. or less, either two Kestners or a regulus centrifugal pump and a Kestner were provided. Each tower, its cooler, pump, and upper and lower feed-tanks formed a closed system, and as the acid fell in strength, it was reinforced by the admission of stronger acid from the next tower, through the regulus valves or, in the case of No. 3 tower, by fresh concentrated acid.

Next in order was the series of three final filters—Nos. 3, 4, and 5. These were in all respects similar to the two which have already been described and figured, except that the gas in each of the three was delivered to the space under the coke and found its way up to the top. The drains from all five filters ran into the same launder. From these filters the gas (now presumed to be free from acid or moisture of any kind, and therefore not to be liable to contamination by contact with iron) was conducted in a 30-in. steel pipe to the pressure equaliser which stood before the blower. This consisted of a steel cylindrical shell 5 ft. in diameter and 6 ft. deep, with cast-iron conical ends to which the 30-in. pipes were connected at top and bottom. Inside were three diaphragms perforated with $\frac{1}{2}$-in. holes. The function of this piece of apparatus was the reduction of the pulsations on the suction side of the blower, which are apt to damage the lead sides of the last filter by causing the sheeting to vibrate. In this the equaliser was not very successful, and it was generally necessary to add more bearers to the filter in question. The perforated plates were also liable to be blocked by frozen acid in cold weather, and a small pipe by which hot gas could be passed in to reduce the "chokes" was found a useful addition.

The Conversion System.—The blower was of the Roots type, and had a capacity of about 30 cub. ft. per revolution.

It was driven at about 160 r.p.m. by a 60 h.p. three-phase motor, running at about 600 r.p.m. In order to be able to regulate the volume of gas passing, a 10-in. by-pass bearing a gate valve was fitted between the inlet and outlet pipes of the blower. This allowed of any degree of regulation, and though of course consuming some power, was an invaluable aid in operation. The glands of the blower were packed with Garlock packing, and compressed air, reduced to 5 lb. per square

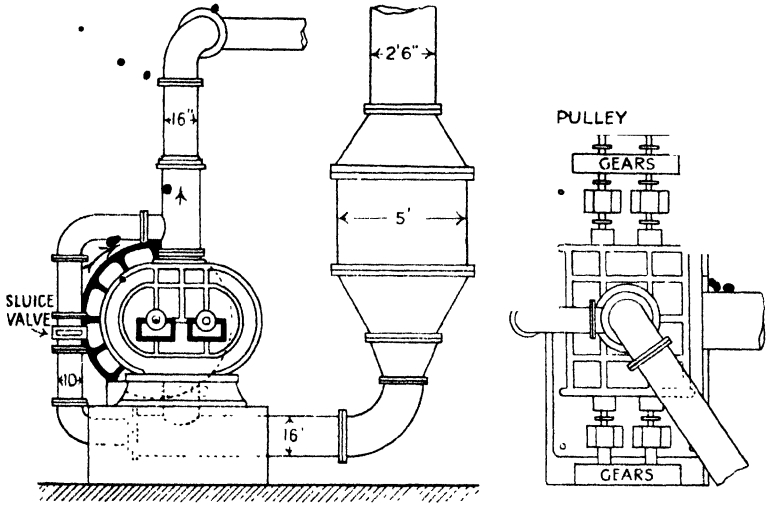


FIG. 88.—Blower and Equaliser.

inch pressure, was used on the glands when necessary to prevent escape of gas. The general arrangement of the blower and equaliser is shown in Fig. 88.

From the blower a 15-in. steel main connected with the grease-catcher. This vessel also acted as a separator for mist which reached the blower and was agglomerated by the mechanical action of the impellers, and consisted of a steel cylinder 30 ft. long and 8 ft. in diameter. At the bottom was a grid of special cast-iron firebars on which was placed a coke packing somewhat similar to that of the filters. The gas entered the space below the grid, passed upwards and left at the further end; a drain and lute were provided. In ordinary circumstances no oil came from the drain; probably little ever left the blower, but the amount of acid caught was

ways considerable. The 15-in. steel outlet pipe was continued along the side of the converter house, and from it two 10-in. branches fitted with gate valves led the cold gas to the two heat exchangers which formed the first section of the regenerative system.

The course of the gas-streams and the arrangement of the plant can be seen in plan and elevation in Fig. 89. The branches from the main 15-in. pipe were fitted with valves that served no particular purpose. The heat exchangers were of the design figured in Fig. 38 in the discussion of preheating apparatus. They contained 104 tubes of 2½-in. bore and 8 ft. 3 in. in length. The cold gas passed through these tubes, and as it was sometimes by no means mist-free, occasional trouble arose from corrosion, resulting in a leakage of this gas into the converted gas inside the tubes, which was of course at a lower pressure. Given quite dry gas, in which case sulphating is more to be feared from the converted mixture, it is probably preferable to pass the converted gas into the inside of the tubes, where any deposit can be punched out.

After the exchangers the two streams of gas united and were carried back to the "heater-cooler" adjacent to the sulphur-burners. This is shown in Fig. 90, and has already been mentioned. In each of its two compartments were suspended three rows, each containing eight U-pipes of cast-iron, about 9 ft. 6 in. long overall, and of 5-in. bore. These pipes were of the form shown in the sketch, and were suspended from steel channels placed on the roof of the chamber by tie-bolts which passed through the upper flange-plate and a similar plate cast on each tube lower down. This lower plate also served as a support for the tiles with which the chamber was roofed, and the space above them was filled in with insulating material. In this way the joints and the suspension were placed entirely outside the hot zone, and any tendency to crack or open on account of expansion or contraction was avoided. The tubes of each compartment were connected to a header having three branches. The method of setting the pipes will be apparent from the sketch. It is worthy of note that, compared with the rest of the plant, this section of it was, so far as the gas to be heated was concerned, too small, and offered a resistance higher than any other element. The rise in temperature due to passage

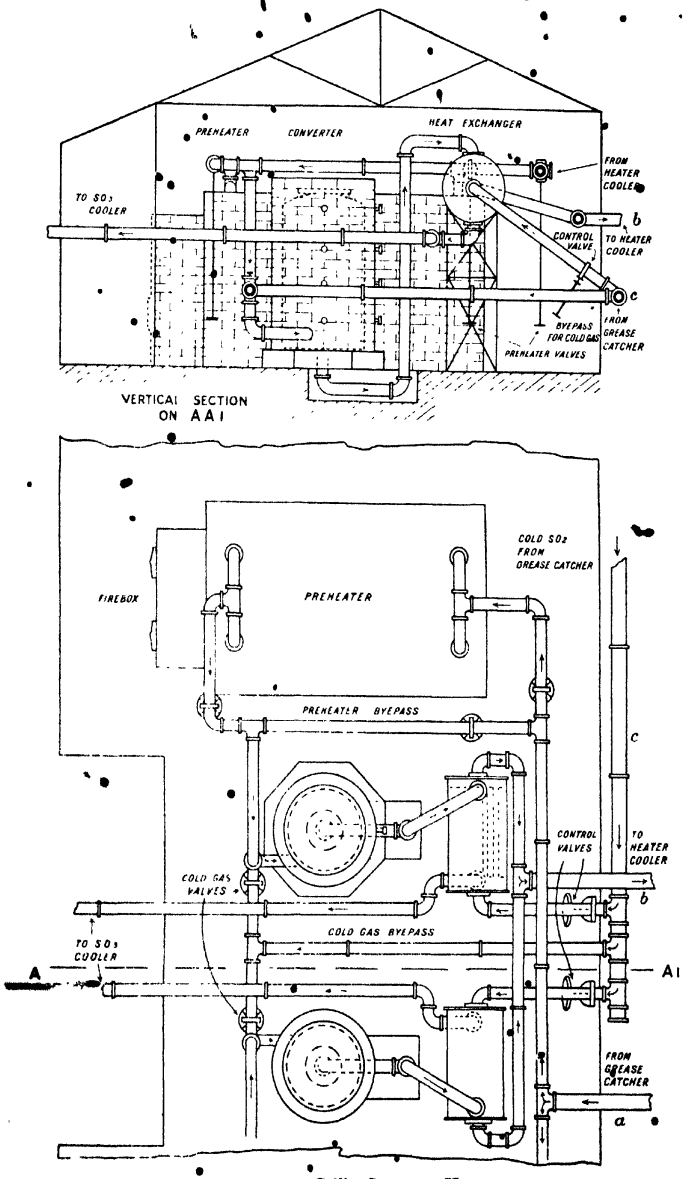


FIG. 89.—Grillo Converter-House.

through the "heater-cooler" was about 140°, *e.g.*, from 180° to 320°. The internal heating area of the pipes below the roof was 1104 sq. ft.

Returning to the converter-house (Fig. 89) through a 15-in. main (all pipes here, as elsewhere, being of steel), the gas divided into two 10-in. branches which led, either directly to the converters, or first of all to the preheaters, each converter having its own preheater. By means of gate valves having long handles to enable them to be worked from the floor level, the preheaters could be by-passed at will, either wholly or partially. It was found that in ordinary circumstances no preheating was necessary once the plant was well under way, and the gas then passed directly through the by-pass to the converters, entering them tangentially. The gas often returned from the "heater-cooler" indeed, with so much heat that the temperature in the converter had to be reduced by partially cutting out both "heater-cooler" and heat exchangers. The "cold gas valves" by which this could be done are shown on the sketch at each converter. The construction of each preheater was exactly similar to that of the "heater-cooler," and each contained the same number of pipes, the only exception being that each preheater was fitted with a firebox for coal, and, between this and the compartments containing the pipes, a common combustion chamber communicating with them by vertical slits in the dividing wall. The flues from the preheaters were carried underground to the single steel chimney of the double unit (4 ft. wide, 65 ft. high) to which, as may be seen from the plan of Fig. 82, the flue from the sulphur-burners also led.

The converters were of the regenerative type, and contained four layers of magnesium sulphate mass each of about 2250 lb. (anhydrous weight), the average platinum content being 0·31 per cent. There were therefore from 55 to 56 lbs. of platinum in the two converters of a unit. A very usual arrangement was to have a top layer of 0·35 per cent. and four lower ones of 0·30 per cent. For a comparison of these amounts with those holding on other Grillo plants, the table in Chapter IV., p. 126, showing the duties of the mass in various cases, may be consulted. Each layer of mass was about 15 in. deep.

The construction of the converter may be seen in Fig. 91. It consisted of an inner and outer shell, the inner one—6 ft. 6 in. in diameter and 12 ft. 8 in. high—being closed at

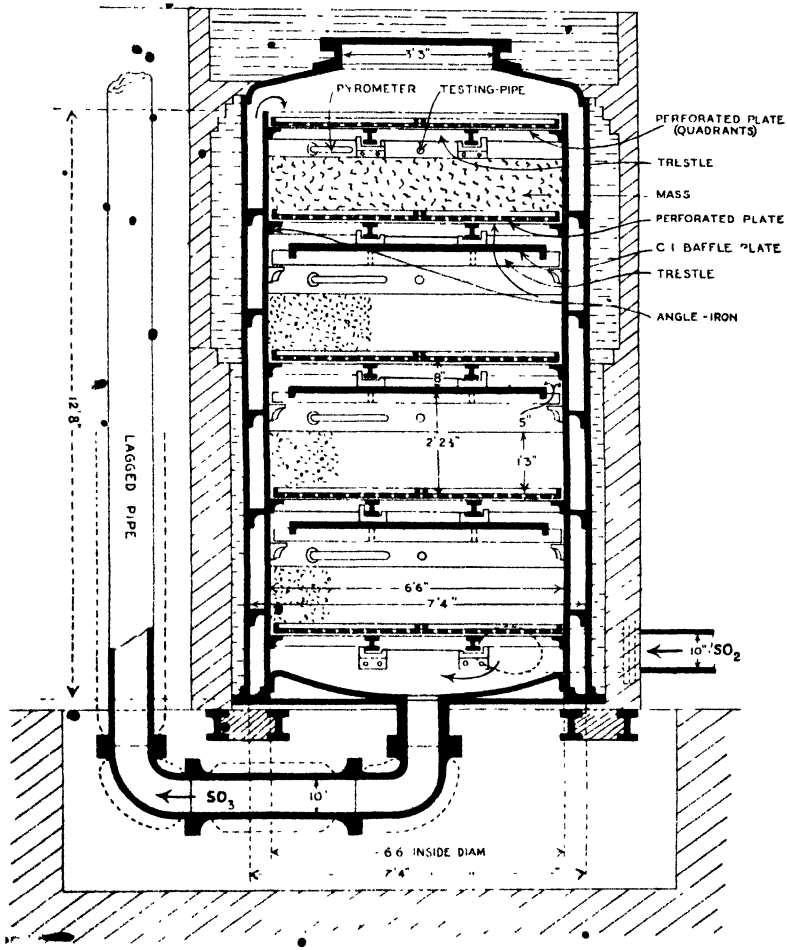


FIG. 91.—D.E.S. Grillo Converter (Sectional Elevation).

the bottom by a dished plate. Between the inner and outer shells were fixed a series of annular baffle-plates with vertical extensions, so that the gas entering tangentially at the bottom through the 10-in. pipe was forced to take a zigzag course, first round for about 280°, then up, round again and so on, until

it finally streamed over the upper edge of the inner vessel and passed downwards, having gained in temperature by 40° or 50°, say from 320° to 370°. This has already been illustrated diagrammatically in Fig. 27. At the top was a perforated steel plate made in quadrants and laid on a circular angle-iron bracket and on a light steel trestle, the ends of which were placed in sockets on the inner wall. This plate acted as a distributor, and was usually covered with a layer of unplatinised mass to act as a filter for any accidental dust or scale. Between each pair of layers of mass was suspended a cast-iron baffle-

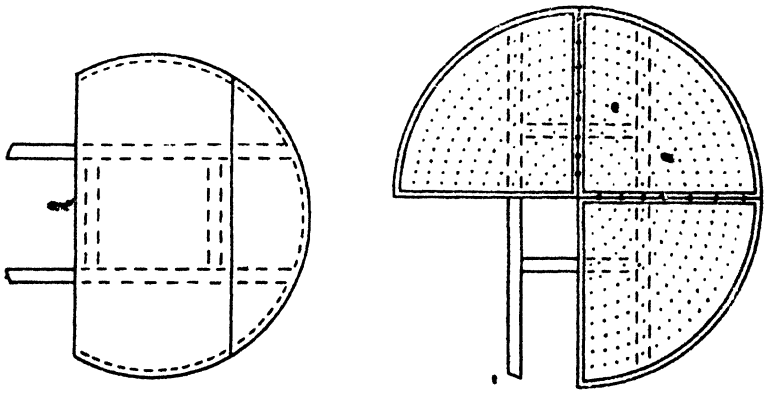


FIG. 92.—Method of supporting Grid- and Baffle-plates in Grillo Converter.

plate. The gas leaving the first layer was thus compelled to spread outwards and strike the inner wall, assisting the heat transference to the incoming colder gas, and being at the same time thoroughly mixed. Fig. 92 shows the method of setting the perforated plates and baffle-plates. Pyrometer pockets were inserted just above each layer of mass. The whole converted was surrounded with a brick casing and the space between was filled in with kieselguhr or slag-wool. It will be understood that all the pipes conveying hot gas, until it left the heat-exchange system, were efficiently lagged. Leaving the converter at about 420° the converted gas passed immediately to the heat exchangers, passed over the tubes and then, at a temperature of 260° to 280°, to the "SO_3 coolers" through 10-in. unlagged pipes, one for each exchanger.

There were two of these coolers for each unit, built side by

side in a shed adjoining the absorption-house. Each consisted of two ranks of eight 6 in. tubes 30 ft. long, coupled at one end to 10-in. inlet and outlet headers, and at the other end to return bends. The total cooling area, excluding headers, was for each cooler 840 sq. ft. Water pipes were arranged for spraying the coolers, and the floor of the shed consisted of a leaden tray for draining. In order that any condensate in the pipes might run out, the outlet headers were set 6 in. lower than the inlets.

The temperature desired for the gas leaving the coolers was from 60° to 70°. To secure this on high charges, with water cooling, the arrangement was amply sufficient. Air cooling, however, was generally preferred when possible. On low charges and in starting-up the coolers were a source of danger, owing to the difficulty of working without blocking them up with solid trioxide; and in one instance it was necessary to provide for warming them in cold weather.

The Absorption System.—The 10-in. main leaving each section of the "SO_3 cooler" was connected to a series of three absorption towers 24 ft. high and 6 ft. in external diameter, the six towers of a unit being supported on a reinforced concrete platform about 7 ft. high. The gas entered at the bottom of two towers (Nos. 1 and 4) and left at the top of two others (Nos. 3 and 6) by pipes which passed upwards through the roof into the air.

A sketch of one of the towers is given in Fig. 93. Each was made of ½-in. steel plate in three sections, and was closed at the bottom by a dished plate of the same thickness, and at the top by a removable flat cover to which was attached a 3-in. fitting for the cast-iron acid sight-box illustrated in Fig. 94. On the bottom of the tower was laid a loose steel plate. The inside of the tower was lined throughout with acid-proof brick about 2½ in. thick and 6 in. square, made with V-shaped edges to fit into each other, and set in acid-resisting cement. At the bottom of the tower this lining was reinforced by courses of heavier brick to a height of 2 ft. 8 in. and on these, and a central cast-iron pillar, the heavy cast-iron grid was placed on which the packing lay. Clean quartz was used, in pieces from 4 in. to 6 in. across, and was filled in to within 18 in. of the top. Just above the top of the packing a cast-iron distributing plate

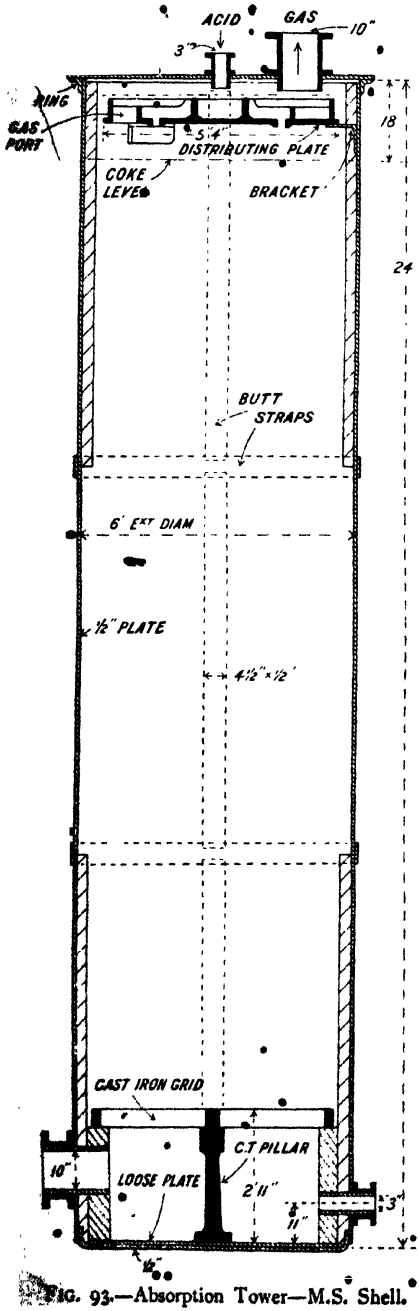


FIG. 93.—Absorption Tower—M.S. Shell.

was adjusted horizontally on three brackets. In the centre of this plate was a cup with serrated edges, into which the acid fell. Flowing over the serrations of the cup it was delivered to the various compartments of the plate, in each of which was a hole, so that there were numerous cataracts of acid at various distances from the centre. There were also several gas-vents in the plate, one of which is shown in the drawing.

For each unit there were three steel acid-circulation tanks 8 ft. long, 5 ft. broad, and 4 ft deep, situated on brick piers about 2 ft. high. There was also a high level tank on a weigh-bridge by which the feed acid could be weighed and fed into circulation, and an oleum receiving tank from which the acid made could be pumped to storage. The acid in the circulation tanks was fed to cast-iron centrifugal pumps through the bottom outlets and pumped to the sight-boxes at the top of the towers, each tank feeding two towers (or four). Returning to the tank, the hot acid ran through coolers which in the case of oleum were of 5-in. steel pipe, and in that of acid of lower strength of 6-in. square-flanged cast-iron pipe. Such a cooler (for oleum) is

shown in Fig. 95. The pipes were supported on racks and connected in the usual way to prevent the formation of air-locks. It was found an advantage to provide splash-boards to make the flow of water between the pipes more even, and in some cases considerable economy of water was effected by spraying the water on to the pipes with spraying jets similar to those used in fire extinction, or in Gaillard towers. The importance

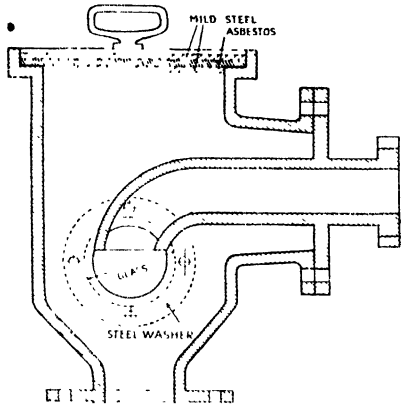


FIG. 94.—Sight Box for Absorption Tower.

of securing adequate acid cooling cannot be overrated, and it was found necessary in all plants to increase the cooling area to much more than the original amount. The results of insufficient cooling on all but the smallest charges were bad absorption and rapid destruction of the plant.

The system of circulation and the consequent connections differed considerably from one plant to another, and naturally varied with the nature of the feed and of the acid required. At Gretna, where 92 per cent. sulphuric acid was for the most part used as feed to make 20. per cent. oleum, circulation

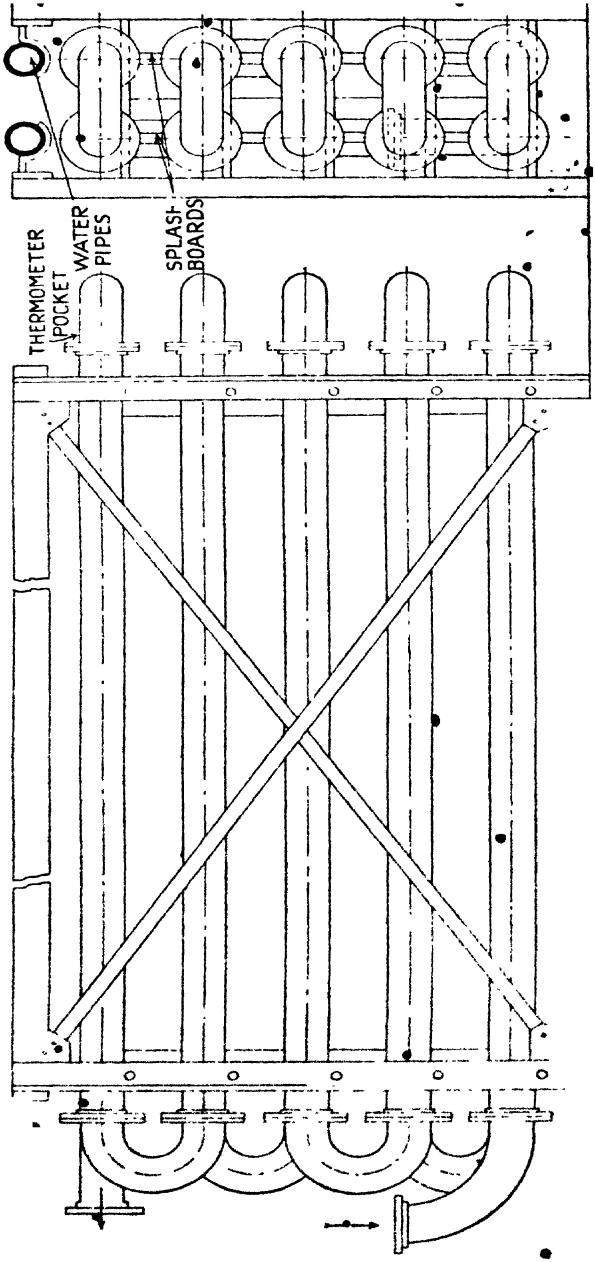


FIG. 95.—Acid Cooler—5-in. Steel Pipe.

was carried out from all three tanks, and the arrangement was that shown in Fig. 96. Feed acid flowed into No. 3 feed-tank, and through a $1\frac{1}{4}$-in. cast-iron bottom connection was allowed to run to a Rees-Roturbo cast-iron pump with an 8-in. impeller direct-coupled to a 4 h.p. totally enclosed motor), which elevated

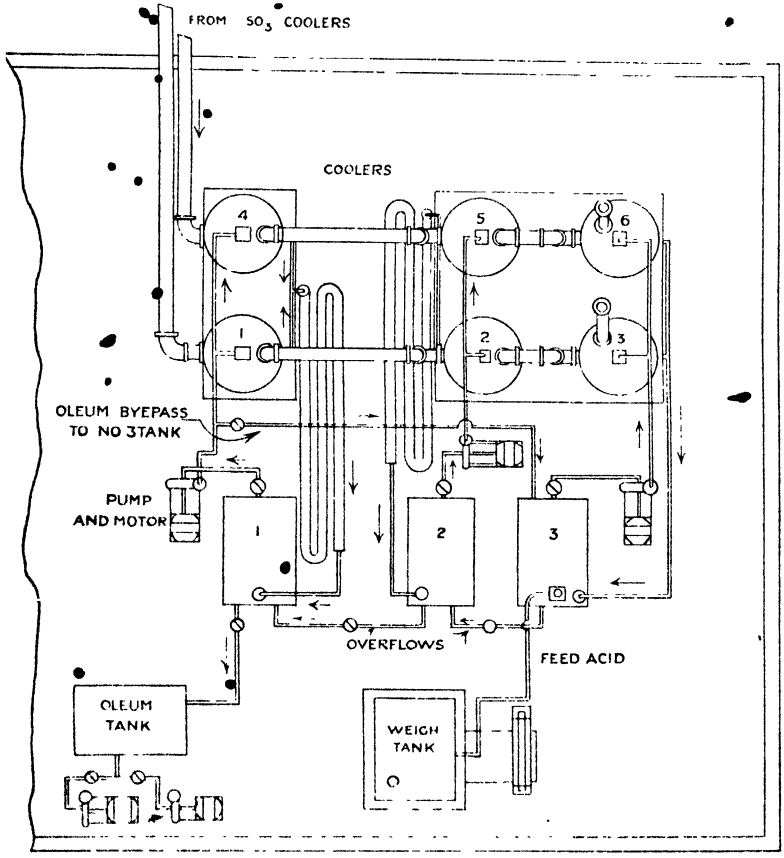


FIG. 96.—Absorption System—Gretna.

it through a $2\frac{1}{2}$-in. oval-flanged cast-iron pipe to the tops of towers 3 and 6, about 8 tons of acid being fed through each tower per hour. This acid returned directly to the tank from which it came. At the same time, by means of a 3-in. overflow pipe, a certain proportion was overflowing into No. 2 tank, which was fitted with a pump and circulating pipes to and from towers 2 and 5, with the addition of a cast-iron acid

cooler. No. 1 tank was connected in the same way to towers 1 and 4. In this instance the delivery and return pipes were of steel and the cooler, also of steel, was 20 ft. long, with two ranks each containing five pipes, *i.e.*, similar to Fig. 95, but twice as long. From No. 3 tank the oleum ran, also by overflow, to the stock tank from which it was pumped to the battery of 30 ft. × 9 ft. storage "boilers."

In the short discussion of circulating systems which has been given under "Absorption," the defects of this particular system have been pointed out, and it was in fact found necessary to provide a by-pass from the rising main of No. 1 pump, to allow oleum to flow into No. 3 tank, for without this the acid could not be brought to the necessary strength of 98 per cent., the overflow from No. 1 remaining at 20 per cent. SO_3. When these conditions were established, the acid in No. 2 was from 99 to 100 per cent. H_2SO_4. The whole system worked well and gave little trouble; it has the advantage that if any pump or circulating pipe is temporarily out of action, the two tanks which are unaffected, with their towers, are sufficient to maintain absorption at the usual rate.

Another and a better arrangement, employed at Queen's Ferry and elsewhere, connected circulation tanks Nos. 2 and 3 together, and fed the last four towers from No. 2 tank, the run-off from these towers falling into No. 3, and from there passing to No. 2. In this way there were only two strengths of acid in circulation—20 per cent. oleum in No. 1 and 98 per cent. in Nos. 2 and 3. An overflow pipe from No. 2 to No. 1 was provided as usual. Very large coolers—with from 500 to 800 ft. run of pipe—were provided, and in some cases were housed outside the building under the "SO_3 coolers." An example of this design is seen in Fig. 97, which represents a single unit plant (East Greenwich). For the oleum section of the plant (towers Nos. 1 and 3), steel pipes and coolers were in use for the 98 per cent. acid section, and cast-iron for the remainder. The outlets from the towers were connected directly to pipes of the same diameter as the coolers (5 in. and 6 in.). The rising pipes were of 2½-in. bore. Feed acid could be run as usual into No. 3 tank or, when no feed acid was available, water could be added at the mixing head of the cast-iron cooler on the right-hand side. The centrifugal pumps were of the vertical, glandless

type already illustrated in Fig. 77. The cast-iron acid valves were also specially made for this work and proved very

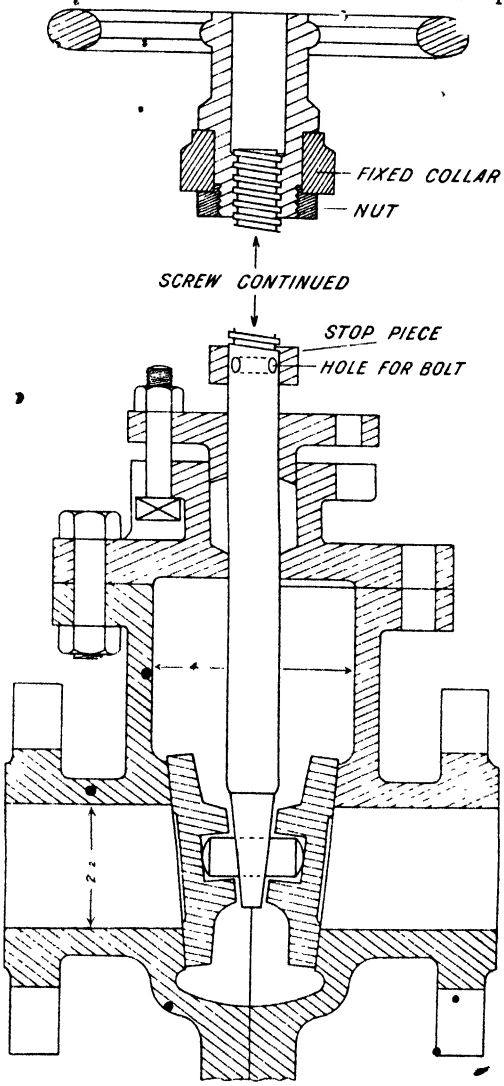


FIG. 98.—2½-in. C.I. Acid Valve.

satisfactory. They could be opened to the full bore of the pipe and showed no tendency to jam or stick. Fig. 98 shows a section of the 2½-in. valve. Of all the alternative arrangements

of the absorption-house, this, for the production of 20 per cent. oleum, was probably the best.

Between the towers Nos. 1 and 4 will be noticed, in Fig. 97, a small cast-iron tower connected to the "SO_3 cooler" by a separate pipe. This was the auxiliary tower which, on a single unit plant, was necessarily used for making pure acid for the scrubbers. Acid was circulated round this small tower (brick-lined like the rest) from the tank immediately to the left of it and ran back to the tank by way of a mixing pot (shown in plan and elevation), into which the necessary water could be added, in order to keep the acid at 98 per cent. The tower was only in occasional use, and to avoid the use of a valve which in these circumstances and in the constant presence of trioxide is extremely apt to seize, a lute was fitted which could be filled with acid and emptied at will. The lute was a cast-steel T-piece as shown in Fig. 99. By allowing acid to flow in, the gas current could be cut off. When the tower was required for use the acid was drained out, thawing with a blow-lamp if necessary.

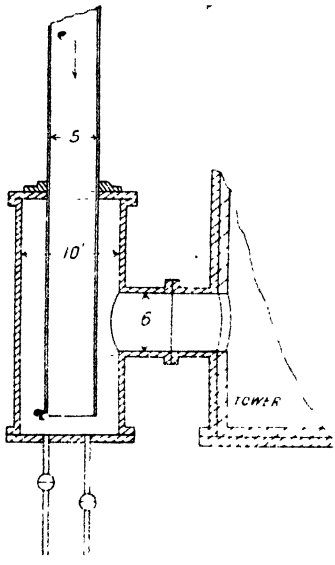


FIG. 99.—Gas-Lute for Auxiliary Absorption Tower.

2. Operation.

Charging and regulating the Burners.—In the operation of the burners, the important points were those of obtaining (*a*) complete combustion, *i.e.*, no "sublimation"; (*b*) a high temperature in the outlet-flue and "heater-cooler"; (*c*) a constant percentage of dioxide.

(*a*) The charge of sulphur per burner per hour varied from 50 to 90 lb. (or from 6·4 to 11·6 tons per unit per day). It was dropped into the pan from iron scoops through the sliding door, the whole twelve burners being charged each hour in a definite order. The sulphur melted on the bottom

of the hot pan and then was partly burnt and partly boiled away into the chequer-work, the slides in the door being regulated until only sufficient air was being drawn in to cause the charge to require, in appearance, fifty-five minutes for burning. The secondary air-vents in the air-flue were kept fully open, and in ordinary circumstances admitted sufficient air to give an almost colourless flame at the level of the chequer-work inspection door (p_2, Fig. 83). No other air-vents were required if the draught in each burner was equal.

(*b*) To assist the heat regeneration of the plant, the "heater-cooler" had to be kept hot, and for this purpose a temperature of 650° or more in the flue leaving the burners was required, and to obtain it the average dioxide percentage in the burner-gas was held as high as possible — usually between 8 and 11 per cent. As 5 per cent. gas was used at the converter, the additional air required was admitted at some point in the purifying system. In ordinary practice these figures may be raised with care to 10 and 13 per cent., without danger of unconsumed sulphur being carried away. Special care is necessary when cleaning out the pans. This was generally done about twice a week. The main doors of two burners were fully opened, and the dust removed as quickly as possible. So much air then entered at these doors that an insufficient amount might be carried into others and "sublimation" ensue. To guard against this, it was usual to reduce the charges shortly before cleaning began. Once hot, the pans and brickwork retained their heat for a very long time. The plant could be shut down for three or four days and restarted without trouble.

(*c*) To obtain the greatest possible constancy of gas composition, it was first of all important to adjust correctly the by-pass slides between the two flues (S, Fig. 83), so as to have the same suction in each fire. The correct setting was that in which each slide was less open than that lying adjacent to it, and further up the gas stream in the flue (G_1, Fig. 83), and it could be checked by observing the time required for each fire to burn out, or better, by actually measuring the suction at each burner door with a very delicate manometer. With sulphur charges of 65 lb. the suction was equal to about 0·170 in. of water, and did not vary from one pan to another more than 0·01 in. There was in general, however, and in spite

of such precautions, a slight increase of suction in one direction or another along the burners, which caused the fires, taken in order along that direction, to burn out increasingly fast.

It was therefore advisable that the order of charging should be arranged to counteract, if possible, the effects of this regular variation in suction, and the order adopted finally was therefore the following :—

	Fires.											
Mins.	1.	2.	3.	4.	5.	6.	7	8.	9.	10.	11.	12.
0	×	...	...	...	...	...	...	...	...	...	...	×
10	...	...	×	...	...	...	...	...	...	×	...	...
20	...	...	...	...	×	...	...	×	...	..	...	...
30	...	...	...	...	...	×	×	...	...	. .	...	...
40	...	...	...	×	...	...	...	...	×	...	...	...
50	...	×	...	...	...	...	...	...	...	...	×	...

The fires charged in this order are symmetrically placed with regard to the centre of the burners, and the effects of the pressure gradient were minimised. The composition of the gas entering the converter did not vary more than 0·5 per cent., and for 90 per cent. of the time was much more constant. With any other order tested before this one, the variation was much greater.

In Fig. 100 are given the results of some series of tests made by testing the gas leaving the burners every two minutes for periods of an hour. Graphs III. *a* and IV. show the effect of charging in the way mentioned, particular attention being given to punctual and rapid charging. Graphs I. *a* and II. *a* represent other methods. It may be mentioned that if the charging were allowed to become in any way irregular, or the dampers or slides were at all out of adjustment, the fluctuations were much greater than those shown in the graphs.

The oscillations of all the curves are periodic. The combustion of sulphur in a hot pan is not a regular process, and the cause of the oscillations became clear on studying individual fires. Samples were withdrawn from the chequer-work, and the same main features appeared in each case. The sulphur was melted and well alight in ten minutes after charging. The dioxide percentage then rose rapidly (to 9-12 per cent.), and a

sharp peak appeared in the graph at about twenty minutes after charging. The percentage then fell rapidly and the graph showed that combustion was practically over at forty minutes

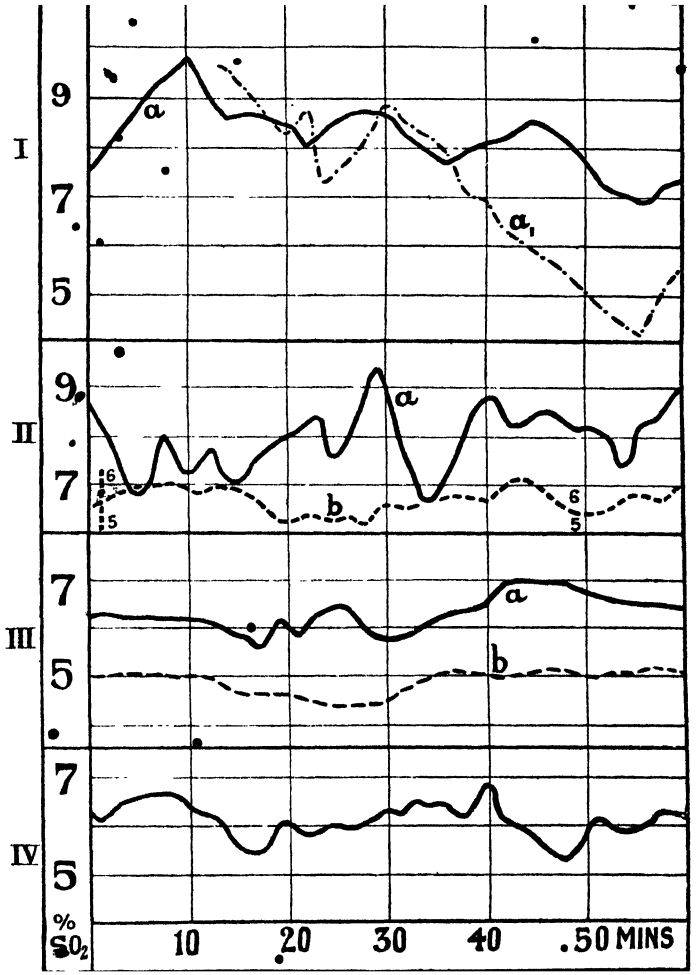


FIG. 100.—Fluctuations in Burner-Gas Composition.

past, although the fire appeared to the eye to be burning almost to the time of the next charge. This conclusion was confirmed by omitting a pair of charges from two fires during an hour's run. The crest usually produced fifteen to twenty minutes after charging was absent and a trough present instead. (See

Graph I. a_1, obtained when a pair of charges was omitted at thirty minutes past the hour.)

Each of the graphs may therefore be considered as the resultant of six single graphs added together, each representing a pair of fires burning effectively for about twenty-five minutes of the hour. The oscillations are occurrences which clearly are to be expected in this or any similar plant.[1] Several variations were tried in the hope of causing the fluctuations to neutralise each other, but with no real success. The result of one of these is shown in Graph II. In this the charges were only half the usual amount, but were put on twice as often, so that Nos. 1 and 12 were charged at 0 and 30 minutes, Nos. 2 and 11 at 5 and 35 minutes, and so on. The graph shows a half-hourly cycle, with an interesting alternating form. In each case *a* is the burner-gas and *b* the converter-gas curve. The fluctuations were to some extent damped down by the effect of the large gas volume of the "heater-cooler," and by the admission of the secondary air for dilution, but were nevertheless always repeated at the converters from fifteen to twenty minutes after the time of their passing the burner-flue. This had a certain effect on the conversion, which will be detailed later. These facts constitute, alone, a very forcible argument in favour of mechanical burners.

The Working of the Purification System.—The acid in the last scrubbing tower was kept at 93 to 95 per cent. by the admission of fresh acid of 98 per cent. (or in some cases of oleum) to the circulation tank of this tower, excess acid being passed to No. 2 tower and thence to No. 1 as required. The strengths of the acids in these two towers remained at constant figures, which depended on the amount of trioxide formed in the burners, and on the atmospheric moisture drawn in. With a high burner conversion of say 4 to 5 per cent., and in cold weather when the atmospheric moisture was low, the contents of No. 1 tower might remain at 80 per cent. and if they were diluted, increase in strength afterwards, owing to the absorption of stronger acid mist. More usual figures were: No. 1, 65 to 70 per cent., and No. 2, 80 to 85 per cent. When chlorides were suspected in the sulphur, No. 1 was daily diluted to about 50 per cent. by the addition of water, and renewed entirely at

[1] Miles and Sarginson, *J. Soc. Chem. Ind.* (*Trans.*), 1922, 41, 183.

frequent intervals. In extreme cases sprays of water were set in two of the pipes of the "SO_2 cooler." This entailed a loss of production of about 1 per cent., and was resorted to only as an extreme measure. The effect of chlorine on the conversion has already been discussed in the chapter on Gas-Purification.

The course of the purification can be traced partially by examining the amounts of sulphuric acid and of "total moisture" (*i.e.*, H_2SO_4 and H_2O) carried by the gas, in the table of representative data given towards the end of this section. It will be seen that although the first filters and scrubbers accounted for most of the mist, its elimination after this was gradual, and that the blower and grease-catcher caught a considerable fraction of what remained. The gas leaving the grease-catcher contained 0·010-0·020 gm. per cubic metre of total moisture if the purification was working normally.

On all plants tests were run for a week or more to ascertain by actual measurement, so far as possible, the actual amount and composition of acid eliminated by each part of the system. As an instance, the result of one made at Gretna in May 1917 is given in the table below. During the period 45·7 tons of

Part of Plant.	H_2O.		SO_3.		Acid.		
	Tons.	Per cent. of Total.	Tons.	Per cent. of Total.	Tons.	Per cent. of Total.	Per cent. H_2SO_4.
Caught in SO_2 Coolers . .	0·190	4·0	0·200	6·1	0·39	4·9	62·7
„ „ No. 1 Filter . .	1·620	34·4	1·430	44·0	3·05	38·3	57·5
„ „ No. 2 „ . .	0·600	12·7	0·450	13·8	1·05	13·2	58·2
„ „ No. 1 Scrubber . .	0·460	9·8	0·030	0·9	0·49	6·2	} (37·3)
„ „ Nos. 2 and 3 Scrubbers	1·620	34·4	0·880	27·1	2·50	31·4	
Passing from Scrubbers* . .	0·210	4·7	0·260	8·1	0·48	6·0	(66·5)
Average or Total . .	4·710	100·0	3·250	100·0	7·96	100·0	50·0

* Calculated.

sulphur (97·8 per cent.) were burnt, containing 0·15 per cent. of water. The average percentage of dioxide in the converter-gas was 5·11. On each day estimations of atmospheric moisture were made by the chemical test. The average gave 464 lbs. in a million cub. ft., or (at 10·3° C.—the average temperature)

a saturation of about 78 per cent. The water drawn in with the air used for combustion and conversion can be calculated as 4·60 tons and, adding that in the sulphur, the total is 4·67 tons. The amount actually recovered was 4·71 tons.

The first two filters remove about 47 per cent. of the total water and 58 per cent. of the sulphur trioxide generated, and play a most important part in the purification. The scrubbers remove 44 per cent. of the water and 28 per cent. of the trioxide, 4·7 per cent. and 8·1 per cent. respectively, passing on to the rest of the plant. The total of 4·71 tons of trioxide represented 2·91 per cent. of the total production of the plant. What proportion of the mist was passing from the scrubbers into the final filters could not be found directly, for the drip from these, if any, gives no guide to the amount of acid they are taking up. The lowest entries in the table were, therefore, calculated from gas-tests.

The inclusion of two filters before the scrubbers justified itself amply, and on some plants the recovery of trioxide by these means was as high as 67 per cent. That so much could be eliminated before the scrubbers were reached proved in the end a most important fact. There was also some ground for believing that the more concentrated was the acid in the mist, the more readily was it eliminated by filtration.

At one large factory, the filters had been too loosely packed, and the amount of total moisture in the gas leaving the grease-catcher was on some units as high as 0·80 gm. per cubic metre. Although this gave no serious anxiety so long as a good grade of sulphur was to hand, it was a most undesirable state of affairs. Various experiments were made. The third and fourth filters were sprayed at regular intervals; this had a slight favourable effect. The feeds to the scrubbers were doubled; the amount of moisture rose to 1·50 gm. Finally, it was found that if the burner-gas was made as concentrated as possible and carried to the first filters without any addition of secondary air, an acid of well over 90 per cent. ran from these filters, and the whole purification became more complete. In adopting this method the inlet for the secondary air was removed from the "SO_2 coolers" to the inlet to the second scrubber, so that the system up to this point had to deal only with the comparatively small volume of burner-gas containing from 10 to 12 per cent. of

dioxide. The secondary air was drawn in through a duct connected to the tops of the scrubber circulating tanks, so avoiding a small loss of dioxide which, even with covered tanks, was otherwise appreciable. The temperature of the burner-flue then rose to 750° or 800°.

The chief condition of successful filtration is to have the largest possible amount of fine coke—between $\frac{1}{8}$ in. and $\frac{3}{16}$ in. —carefully dried before putting in. Trouble was encountered in the same measure that this provision was diminished or neglected.

Operation of the Converters.—In running the converters, there were three conditions to be established in order to secure the highest possible efficiency. It was necessary to maintain (*a*) delivery of gas to each converter at a constant rate; (*b*) a suitable percentage of dioxide as nearly constant as possible; (*c*) appropriate and steady temperatures at the inlet and in each layer of mass.

(*a*) A constant rate of flow presented little difficulty; the motors driving the blowers were practically invariable in speed, and slipping of the belts was rare. It was usual to open or shut the blower by-pass valve in accordance with the indications of the water manometer on the delivery side of the blower, maintaining a constant head of from 40 in. to 60 in. of water, according to the charge. A better method, however, was to work by a manometer attached to the converter inlet, for the resistance of the plant subsequent to this point might be considered invariable, whereas the resistance of the whole plant after the blower, as indicated by the gauge at the blower outlet, was liable to alteration. If, for instance, the "cold gas" by-passes were opened, the resistance of the plant as a whole fell, the blower continued to impel the same amount of air as before, but a greater proportion went through the plant, and a smaller one through the blower shunt. The pressure at the converters consequently rose, and the gas concentration fell.

(*b*) To keep the concentration constant was a more difficult matter. It has been seen that the intermittent charging of the burners gave rise to fluctuations which were unavoidable with this method of combustion and, when reduced as far as possible, gave rise to corresponding fluctuations of 0·5 per cent. in the converter-gas. This unevenness of composition was a

considerable hindrance to good conversion, and had the additional disadvantage of making conversion tests more difficult. Some observations of the effect of the variations are given in Fig. 101. In Graph I., curve *b* shows the percentage of dioxide at the inlet, curve *d*, the conversion. When Graph I. was obtained, the inlet gas was more concentrated than was found best. It will be seen that each rise in concentration is followed by a very definite fall in conversion, and *vice versa*. In the case of Graph II. not only are the initial fluctuations smaller, but the mean dioxide percentage is lower also. The result is that the fluctuations are less than before. The higher was the average concentration, the more did a variation by the same fraction affect the result.

Tests were also made on the gas before and after it passed through the first layer, and some results of these are given in Graphs III. and IV. The effect is the same, but is more marked than before. In the first case the conversion (curve *d*) is seen to fall from 40 to 35 per cent. in fifteen minutes. Curve *e* represents the percentage of the initial total volume converted, and is a measure of the *amount* of conversion. As might be expected, this curve rises and falls with the first (*b*), showing that the layer of mass attempts to deal with the extra load due to the influx of richer gas, but (as curve *d* shows) is not quite equal to the task. The same remarks apply, in a lower degree to the converter as a whole, and the discussion may be followed a step further. When the entering gas became rapidly richer, conversion by the first layer fell (by 5 per cent. or so in the example given), and the remaining layers had to deal with an extra load, due not only to the increased concentration but also to the fall in efficiency of the first layer. This fall in efficiency was inevitable, since this layer was not allowed to be hot enough to convert more than 25 to 35 per cent. of the whole. If its temperature were allowed to rise much above this, a far greater catalytic activity was attainable in it; but the whole converter then became so hot that the total conversion, from 96 or 97 per cent., fell to 92 or 93 per cent. For the best result, it was essential to divide the load as evenly as possible between all the layers. This was attained in the ordinary way by making sure that no pyrometer indicated more than 470° or 480°.

These conclusions were confirmed by further observations,

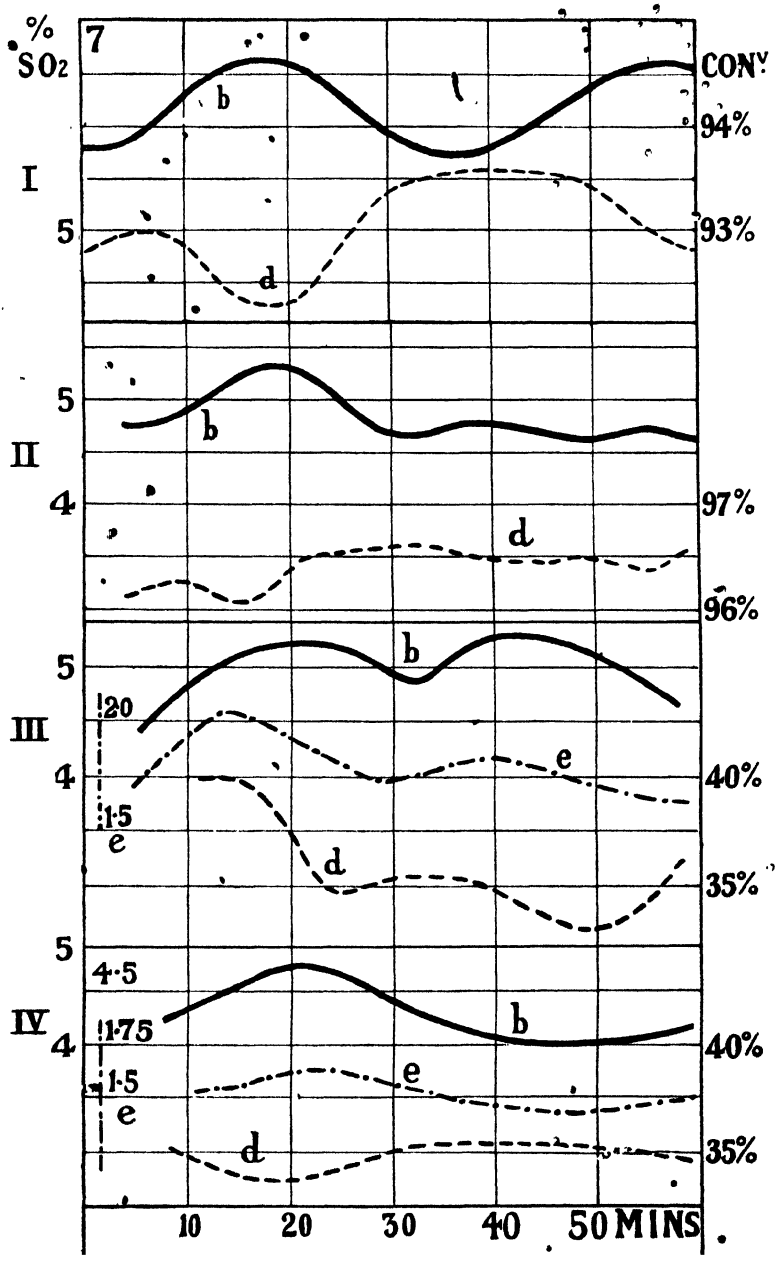


FIG. 101.—Fluctuations in Conversion: I. to II., Total Conversion; III. to IV., Conversion by First Layer.

and Fig. 102 represents the result of a series of tests made during and for some time after the cleaning of a set of burners,

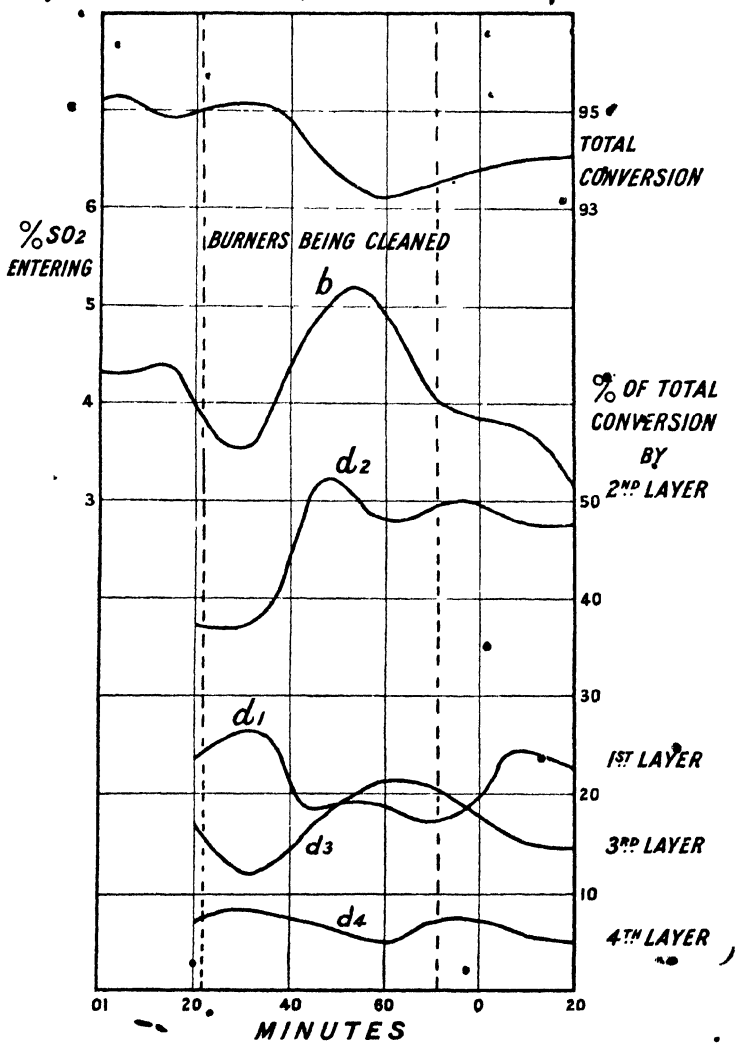


FIG. 102.—Fluctuations in Conversion by Separate Layers of Mass.

an operation which necessarily gave rise, on account of the opening of the burner doors, to very marked fluctuations. The period of cleaning is shown by the two broken lines. In

response to the marked increase in percentage which begins at about thirty minutes (curve *b*), the first layer conversion (d_1) falls, while the second and third layers (d_2 and d_3) accomplish a greater proportion of the possible work. The total conversion has meanwhile fallen seriously, but it begins to increase as the concentration passes the maximum, a series of changes in the layers now taking place which, at least roughly, is the converse of the foregoing.

The whole converter was, therefore, in a state of sensitive thermal balance, in which the catalytic capacity of the platinum at the temperatures employed was exercised to its utmost. It would have been of advantage to isolate one section of the mass from the rest, run it at 500° or 520°, and accomplish 60 to 70 per cent. of the conversion in one stage. The remaining three layers would readily have accomplished the remaining conversion, the gas being cooled by heat exchange during its passage between the two sections. This would have made possible the use of a stronger gas than could be used in the existing converters with efficiency.

The most general limits for the gas concentration were 4·5 and 5·5 per cent. To obtain the best possible result—about 97·5 per cent. — which was attainable only on comparatively low charges, even lower limits, 4·0 to 5·0, were advisable. Charges up to 100 lb. (31·8 tons trioxide *per diem*) could be burnt with a conversion of from 91 to 92 per cent.

(*c*) The data given in the two foregoing figures were of course the results of experimental work; for the purposes of ordinary control, temperatures were mainly relied on, in conjunction with periodical tests of the conversion. If the temperature shown by the pyrometer just above the first layer were kept at any given figure, the remaining temperatures soon settled down to particular values determined by the gas-concentration and the rate of flow. The preheater was, as a rule, used only for starting-up, and the inlet gas contained, without its use, a more than sufficient reserve of heat. The temperature of entry was, therefore, controlled by opening the "cold gas" by-passes. With low charges (50 to 60 lb.) from 370° to 380° was aimed at. On higher charges, the heat developed in the converter being greater, from 355° to 365° was suitable. If the entry temperature was too low, that of the

gas leaving No. 1 layer would begin to fall, and if the fall were not checked, the second layer would rise in temperature and take over part of the work of the first. Incipient loss of conversion could be stopped by first of all cutting off the cold gas, then by increasing the gas concentration.

Absorption.—To describe the operation of the absorption-house, it is not necessary to add much to the description which has already been given of the plant and its connection. It was

Working Data. (*Charge, 70 lb.*; *Atmospheric Temperature,* 15°.)

Place.	Temp. °C.	Pressure. Ins Water	Mist. Mgms. per 100 litres		Remarks.
			H_2SO_4	"Total Moisture"	
Leaving Burners	680	− 0·15	...	...	8-10 per cent. SO_2
Entering SO_2 Cooler, No. 1 Pipe	270	− 0·40	...	...	Burner conversion 2·5-3·0 per cent.
,, ,, ,, No. 6 ,,	90	...	...	...	...
,, No. 1 Filter	21	− 1·50	400-700	1400-2000	...
,, No. 2 ,,	18	− 1·90	...	...	...
,, No. 1 Scrubber	15	− 2·15	120-350	600-1300	Circulating acid 70 per cent.
,, No. 2 ,,	19	2·20	...	...	Circulating acid 86 per cent.
,, No. 3 ,,	21	− 2·40	...	...	Circulating acid 93·3 per cent.
,, No. 3 Filter	22	− 2·60	20-80	40-200	...
,, No. 4 ,,	19	− 2·85	...	...	...
,, No. 5 ,,	16	− 3·00	...	...	...
,, Press-Equaliser	15	...	16-20	30-60	...
,, Blower	15	− 3·70	..	...	...
,, Grease-Catcher	30	+ 49·40	..	...	...
,, Heat-Exchanger Pipes	25	42·00	1-5	10-25	15 ins. drop in pressure due to heater-cooler pipes
,, Heater-Cooler Pipes	185	27·00	...	...	Leaving heater-cooler 360°
,, Converter Inlet Pipe	320	20·80	...	...	...
,, ,, No. 1 Layer	370	...	...	...	Conversion 96 per cent.
,, ,, No. 2 ,,	460	...	...	...	...
,, ,, No. 3 ,,	470	...	...	...	...
,, ,, No. 4 ,,	440	...	...	...	...
,, Heat Exchanger	425	13·50	...	...	...
Leaving ,, ,,	275	6·00	...	...	...
Entering SO_3 Cooler	80		...	...	...
,, No. 1 Absorption Tower	47	5·25	...	...	...
,, No. 2 ,, ,,	45	3·30	...	...	...
,, No. 3 ,, ,,	40	1·65	...	...	...
Leaving ,, ,, ,,	38	...	...	...	...

necessary only to maintain a flow of feed acid at the correct rate, to keep the contents of the first and last reservoirs at 20 per cent. oleum and 98 to 99 per cent. acid by a sufficient number of tests, and to see that sufficient of these acids was elevated by the pumps to prevent the acid which ran back from the towers from rising much above these strengths. The work is much facilitated, at least until steady conditions have been established, by using one of the rapid tests which have been described in Chapter II.

When acid recovered from T.N.T. manufacture was in use as feed, silt used to accumulate in the coolers, so that periodically it was necessary to pump them empty and wash them out. The towers also required the same treatment occasionally.

The efficiency of an absorption system in good running order is extremely high, and the main loss is likely to be due to the carriage of acid spray from the last towers into the atmosphere. This can usually be prevented by an alteration of the feeds, but in some cases spray-catching vessels were fitted to the outlet pipes. Occasionally also a certain amount of apparently unabsorbable mist would escape, and it was found that the application of cold water to the gas-coolers had the effect of producing this.

Every effort was naturally made to keep the contents of the circulation tanks as cool as possible, but, however long the coolers are, a certain rise of temperature is inevitable. With the system illustrated in Fig. 97, but with coolers of a different length, having 270 and 1200 sq. ft. for the oleum, and 98 per cent. acid respectively, the temperatures holding were as given below. The size of the first cooler was afterwards increased :—

Charge.	Gas entering Towers.			Oleum.		99 per cent. Acid.			
	1 and 3.	2 and 5.	3 and 6.	Entering.	Leaving 1 and 3.	Entering.	Leaving 2 and 5.	Entering.	Leaving 3 and 6
6-8 tons S.	56°	52°	34°	50°	60°	34°	68°	34°	33°
10-11 „ „	63°	56°	45°	53°	72°	40°	81°	40°	36°

These figures apply to the production of 22 per cent. oleum, from feed acid of 91·5 per cent. In these circumstances, the absorption of trioxide by the oleum constituted, necessarily, about 60 per cent. of the total absorption.[1] The heat development is difficult to determine practically, but was greater in the towers through which the 99 per cent. acid was flowing than in the others. Calculations similar to those made in the section dealing with the thermal effects of absorption in Chapter VII., and from the data given there, indicate that on 60-lb. charges (7·7 tons sulphur per day) about 230,000 C.H.U. are developed per hour in the four last towers, exclusive of some 60,000 C.H.U. given to the system by the hot stream of gas, and about 180,000 C.H.U. in the oleum system, excluding in the same way some 6000 C.H.U. It is, therefore, evident that the cast-iron cooler is justifiably made the more capacious of the two. When oleum was made from water feed with the system of Fig. 97, the relative heat development in the 98 per cent. acid section became even greater. Some by-passing of oleum to the other circulating tanks was then usually necessary (see, however, the footnote on p. 275). On units making 98 per cent. acid from feed acid of 91 per cent. (or from water), the total heat evolved was greater than in either of the foregoing cases, and the cast-iron cooler had to be capable of dealing alone with all this heat, for only acid of 98 to 99 per cent. was then in circulation.

Efficiency.—The over-all recovery which was obtained by the plant varied to some extent with the charge, but, for medium charges of 60 to 70 lb. per burner, was between 94 and 95 per cent., exceeding this slightly in some instances. To maintain this high level the operation had to be carried out with strict attention to detail and unremitting avoidance of all possible loss. It was necessary to watch conversions closely, to see that sulphur dioxide was not being lost by escaping from the scrubbing acid into the air, and that absorption was proceeding perfectly, and so on throughout the system.

The estimations of efficiency which were deduced from the amounts of acid made and received, and relied ultimately on the dips of the acid storage tanks, were occasionally checked by more direct determinations in which all the materials were carefully measured or weighed, and the losses were evaluated directly.

[1] *T.R.E.S.*, 1921, 5, 205.

Some details may be given of one special test carried out in this way. No change was made in the normal working of the unit, but water was substituted for acid as feed, in order to avoid the introduction of a large amount of material extraneous to the plant. A special calibrated storage tank was reserved for the 20 per cent. oleum made, and the temperatures holding at various levels in the tank were determined at the end of the run by using maximum thermometers. At the beginning and at the end, all towers were drained and all service tanks dipped. In the second run all sulphur was burnt out from the burners to begin with, and the same was done at the end. The results of the two runs are shown below:—

DIRECT ESTIMATION OF RECOVERY.

SO_3 recovered in	No. 1 (3 days).	No. 2 (4 days).
Absorption plant . . .	92·49 per cent.	92·30 per cent.
Purification „ . . .	2·30 „ „	2·23 „ „
Total Recovery . .	94·79 per cent.	94·53 per cent.
Loss of SO_3 . . .	5·21 per cent.	5·47 per cent.

DIRECT ESTIMATION OF LOSSES.

SO_3 lost in	No. 1.	No. 2.
Conversion	4·56 per cent.	4·42 per cent.
Circulation of scrubber acid .	0·23 „ „	0·54 „ „
Absorption	0·28 „ „	0·28 „ „
Leakage to drains . . .	Nil	Nil
Unaccounted for . . .	0·14 per cent.	0.23 per cent.

THE UNITED STATES GOVERNMENT PLANT—NITRO, WEST VIRGINIA.

This plant was projected in 1918 to make and concentrate the sulphuric acid required for the production of 300 tons of smokeless (nitro-cellulose) powder per day.[1] It was decided to erect seven units of four "systems" each, the capacity of each "system" being about 16 tons of sulphur trioxide. Construction

[1] Chase and Pierce, *J. Ind. Eng. Chem.*, 1922, 14, 498.

of the first group was begun on 15th March, and was complete on 10th June. At the time of the Armistice four units were complete and the remainder were very nearly so. Sulphur was readily obtainable and therefore chosen as starting material; but it was not known whether the plant should at all times be operated with sulphur, so that more scrubbing apparatus was installed than would otherwise have been thought necessary, and the sulphur burners were so placed that pyrites-burners could be substituted if they were required. From the standpoint of sulphur consumption a little of the possible efficiency was sacrificed in order to economise platinum. To save fuel by installing regenerative converters was not considered worth while, for such plant could not be obtained for a long time. The floor space required for the seven units was about 300,000 sq. ft. The converter buildings had steel frames; those enclosing the absorption plant had timber frames.

A plan and a section of two "systems" (*i.e.*, of half a unit) is given in Fig. 103.

Burners and Purification System.—The sulphur was brought by rail and unloaded into concrete storage-bins and was removed from these to the burners in wheel-barrows. The rotary burners were of the Glen Falls type, 4 ft. in diameter by 16 ft. long. A cast-iron combustion chamber was placed after each burner, and following this was a series of cast-iron gas-cooling pipes (presumably air-cooled). From these pipes the partially cooled gas was led into the first of two scrubbing towers, each made of lead lined with acid-proof brick, filled with quartz, and 8 ft. square by 20 ft. high. Between these two towers there was a water-sprayed gas-cooler consisting of 750 ft. of 16-in. lead pipes, each 45 ft. long, connected in such a way that they formed a coil in a rectangular block four pipes high and four pipes wide. The hot gas entering the first tower was cooled by contact with dilute sulphuric acid running down it, and this acid was at the same time concentrated sufficiently to be passed down the second tower (*i.e.*, to 80 per cent. H_2SO_4). The effluent from the second tower was returned for concentration to the first. The heat of the burner-gas was therefore utilised to some extent, and the gas was scrubbed and partially dried. It is essential for the success of this cycle of operations that

the coolers placed between the two towers should act well. Some difficulty was found in keeping the system in balance; at one time acid would accumulate; at another the addition of stronger acid from the absorbing system was required to prevent the acid in one or other of the scrubbers from falling too far in strength.

From the second tower the gas was led to the coke filter by a leaden pipe. This pipe ran from the top of the tower across the top of the converter building on a steel platform, as may be seen from the elevation in Fig. 103. The coke filter was a lead box 30 ft. long, 12 ft. wide, and 10 ft. high, reinforced with timber, and filled with coarse coke at the bottom, and from 3 to 4 ft. of fine coke at the top. The gas passed from the bottom at one end of the box to the top at the other. Each "system" had one coke filter. Next in order were the mineral-wool filters. Each was of cast-iron 6 ft. in diameter, and was connected to the coke box by a 16-in. lead pipe. Inside it were two lead screens supported by lead covered pipes, and on each screen was a layer of cotton fibre 1 in. thick, and one of mineral wool 8 in. thick. The gas passed downwards through the filter and was discharged into a 16-in. header. Five of these filters were provided. The purification being almost complete, the gas was led through a steel pipe to the bottom of the final quartz-packed drying tower, down which 98 per cent. acid from the 98 per cent. acid section of the absorption system was sprayed. From this it passed to a steel tower filled with coke, in order that any spray carried over from the drying tower might be eliminated. The gas then passed to the blower which had a capacity of 3000 cub. ft. per minute and was electrically driven. That portion of the plant which has so far been described was therefore under suction, the remainder under pressure. Each "system" had its own blower.

Conversion System.—Each "system" was also provided with a double preheater, heated by two gas burners, and comprising two heating chambers fitted with pipes, and two combustion chambers. The gas entered the cast-iron U-pipes from a header running across the front of the heating chamber, and passed out at the back into a similar header. In this way the gas was raised in temperature to about 400°, and was immediately led to the converters. For each "system" there were

four converters of the simple shelf type, each containing five shelves. No attempt was made to economise heat by fitting heat exchangers, for the necessity of rapid construction forbade any elaboration.

The magnesium sulphate mass was sized from 0·25 in. to 0·75 in., and was platinised after sizing, the percentage of platinum varying from 0·15 to 0·30 per cent. The richer mass was placed in the layer through which the gas passed first. As a preliminary to conversion the mass was heated up as usual, with a current of hot air. In ordinary circumstances the gas entering the converter contained about 5·5 per cent. of dioxide.

Absorption System.—The converted gas leaving the converters at 500° to 550° was conducted by pipe lines to gas-coolers, the first section of which was of cast-iron, the second of steel. For each "system" there were 90 ft. of 12-in. cast-iron pipe, followed by 500 ft. of 12·5-in. steel pipe, the whole being joined in one length, and in the steel section, fitted with arrangements for water-spray. These coolers were in the open air close to the absorption-house. The first absorber was a steel shell 5 ft. in diameter and 11 ft. high, brick-lined and packed with quartz. Down this tower was sprayed acid which had previously been used in the final absorbers, and the spraying was continued until each lot of acid had been circulated through the tower about ten times, and had reached a concentration of about 27 per cent. of free trioxide. A second absorber was added later in order to increase this to 40 per cent., and the gas leaving the first was then carried to the second. Oleum of about 16 per cent. was made in the second absorber under this arrangement, and was then concentrated to 40 per cent. in the first. The final absorption was carried out in steel towers 7 ft. in diameter and 15 ft. high, lined with acid-proof brick and filled with quartz. Acid of 99 or 100 per cent. was maintained in circulation round these towers, and also round the final drying system, by means of cast-iron pumps. Coolers for the acid, both for that in circulation and that run off for use on other parts of the factory, were made of comparatively short lengths of 30-in. cast-iron pipe.

There were, therefore, eventually two initial and one final

absorbers for each "system," with coolers. The feed to the absorption system was recovered spent acid from the nitration of cellulose, and with this was mixed the weak acid produced by the operation of the purification plant. The gas at the end of the process passed out to the air through a spray-catcher fitted at the foot of the outlet stack.

The concentrated oleum produced was very liable to freeze in cold weather. It is stated that this difficulty was overcome by mixing it, when necessary, with a prepared mixture of nitric and sulphuric acids.

This plant, and also the great du Pont installations at Hopewell, have now been dismantled.

Grillo Plant of the U.S. Naval Proving Ground.

This plant, a small installation with no regenerative apparatus, and the simplest possible absorption system, was erected in 1907 at the U.S. Naval Proving Grounds, Indian Head, Me.,[1] for the manufacture of acid used in making smokeless powder. It was designed by the New Jersey Zinc Company.

With a rated capacity of 6 tons of ore, it was operated successfully for three years, burning pyrites from New York and Virginia in O'Brien burners. During the two years previous to 1912, Louisiana brimstone was used entirely. The reason for changing raw materials was primarily to increase the capacity without enlarging the plant, and it was hoped incidentally to reduce costs, notwithstanding the large increase in price per unit of sulphur. These expectations were fully realised.

The burner is housed in a detached frame building 19 ft. × 32 ft., with the sulphur store sheds adjacent. A frame building 52 ft. × 60 ft. contains the conversion and absorbing systems. The gas cooling and purifying systems are in the open at the rear of the buildings, in part protected by an open shed.

The Burner is the Tromblés and Paull burner and has been found most satisfactory. It consists of a horizontal cylindrical

[1] Patterson and Cheney, *J. Ind. Eng. Chem.*, 1912, **14**, 723; *Chem. Trade J.*, 1912, **51**, 293.

iron shell 8 ft. long and 3 ft. in diameter with conical ends, revolving on its axis once in two minutes. At one end is a hopper and worm feed with sliding dampers. The other end connects with a rectangular cast-iron box of 37 cub. ft. capacity, provided with sliding damper and vertical cast-iron uptake pipe. This pipe leads to a brick dust-catcher such as is ordinarily used with pyrites-burners. The dust catcher merely cools the gas, as no appreciable amount of sulphur is carried beyond the combustion box.

The burner is rated at 5500 lb. per day, but there has been no difficulty in burning 6000 lb. per day. Before the hopper is filled, the sulphur needs no other preparation than breaking up large lumps with a shovel. When forced along the worm, the sulphur melts just before it is dropped into the body of the burner, and a sufficient amount of melted sulphur is always present to form a complete liquid coating on the inside of the shell as it revolves. The combustion of any sulphur which is volatilised from the cylinder is completed in the combustion box and vertical uptake.

The special advantages of this burner are ease in controlling composition of gas, low cost of upkeep, and freedom from losses. Once in about two months it is necessary to clean out the dross which collects in the cylinder. To do this, or to prepare for a shutdown for repairs in any other part of the plant, the sulphur charge is allowed to burn out completely. Any residue in the cylinder is then easily removed with a hoe. Starting the burner after cleaning, or even when it is cold, is a simple operation and no losses occur.

The Purifying System.—At the exit of the dust catcher, the gas has cooled to a temperature of about 230°. At this point it enters the purifying system, which consists first of 250 ft. run of horizontal lead pipe arranged in tiers in a wooden rack. All gas passes through this length of pipe. This pipe is cooled by a water-spray, and here is deposited a small quantity of weak sulphuric acid formed in burning the sulphur. The acid deposited is, however, slight in comparison with the amount collected at the same point when pyrites was burnt. The lead pipe connects with a large lead-lined box containing coke, and here a further deposit of weak acid is obtained. Up to this point is formed also a slight deposit of carbonaceous

matter from the asphaltic material which the Louisiana brimstone always carries in small quantities.

From the coke box the gas passes to two wet scrubbers in tandem. Each scrubber outfit consists of a vertical lead cylinder with a conical top, about 4 ft. high, a lead pot provided with lead cooling-coils for water, and an air-lift for circulating constantly a stream of sulphuric acid from the pot to the scrubber. The scrubber is divided horizontally by a perforated diaphragm. The acid washes and dries the gas thoroughly, and flows out through pipes in a weakened condition to the pot. A pot holds 2500 lb. of acid, and is constantly strengthened to a gravity of 1·75 by the addition of strong acid. The excess acid formed at this point is collected in an egg, and can be forced by air pressure to the weak acid supply used for the absorbing system. The air-lift was designed to replace the ordinary bubbler formerly used. Only 5 lb. air pressure is used in raising 80 lb. of acid per minute, and the top of the lift is gas-tight, the air being piped to the gas system, so that any loss of sulphur dioxide at this point is prevented.

From the scrubbers the gas passes to a second lined coke box exactly like the first one, and from thence to a pair of dry filters in parallel. Each dry filter consists of three superimposed lead-lined iron trays luted together. Each tray contains a mat of dry asbestos supporting a quantity of slag wool. A reserve set of these filters is kept ready for use, as they require to be renewed about once every four weeks. The entire charge for two filters is 30 lb. of asbestos and 400 lb. of slag wool. The dry filters complete the purification process and the gas is then carried into the main building. Throughout the purifying process the gas comes in contact with no other metal than lead, but beyond this point either cast-iron or wrought-iron is used entirely.

Within the house the gas is first passed through a positive pressure blower, by regulating the speed of which the composition of the entrance gas is controlled, and the movement of the gas through the whole system is completed. Manometers on either side of this blower show a suction of 1·5 in. of water and a pressure of 0·75 in. of mercury.

The Conversion System.—The next stage of the plant

comprises a preheater and converter. The preheater is a series of vertical iron U-pipes and heaters housed in a furnace heated by coal. In this the gas is heated to an initial temperature of 380°, which is required for proper catalytic action by the contact-mass.

The converter is placed close to the preheater, and is a vertical cast-iron cylinder 6 ft. in diameter and 8½ ft. high, composed of five horizontal sections. Each section contains a wire mesh tray for supporting the contact-mass, and a baffle to properly spread the gas. The Grillo contact-mass contains 0·2 per cent. of platinum. A total quantity of 5900 lb. of mass in coarse granules is spread on the trays to a depth of 14 to 16 in., leaving a space of about 6 in. between sections of mass. The gas enters the bottom of the converter and leaves at the top, pyrometer tubes being provided to read the gas-temperature. After the converter, the gas passes through 180 ft. of iron pipe to the absorber. This pipe is air-cooled, in order that the temperature of the gas may be low enough for good absorption.

The Absorption System.—There are a tower absorber, an acid-cooling pipe, weak acid reservoir, mixer, a lead tank for strong acid, a pump, and a collecting tank. The tower is a vertical cast-iron cylinder 15½ ft. high resting on a cast-iron base, the top being covered by a perforated plate. From the centre rises the exit-pipe for waste gases. The tower is lined with acid-proof tile and packed with quartz rock. The gas enters on one side near the bottom. A constant stream of acid is supplied by the pump to the top plate, percolates through the mass of quartz, and passes out at the bottom of the tower to the cooling pipe. This is a horizontal water-cooled U-pipe, one leg of which carries an outflow pipe connecting with the pump and the collector.

The acid supplied to the top of the tower is kept at a temperature of 70°, and has a strength of 99·5 per cent. H_2SO_4. The strength of the acid leaving the bottom of the tower is reduced by the constant addition of a small stream of 75 per cent. H_2SO_4 just before it enters the cooler.

The reservoir for this weak acid, the mixer, and the strong acid lead tank are mounted on a platform in the centre of the building at a sufficient elevation for the acid to run by gravity.

The reservoir is an open lead-lined box holding 1000 gallons. The mixer is a lead pot provided with lead coils for cooling water, and a special mixing pipe in which water and strong acid are brought in contact.

The mixing pipe consists of two heavy $\frac{3}{4}$-in. lead pipes set at an angle of 30°, and held together by a heavy lead sheath burned on to a short length of $1\frac{1}{2}$-in. lead pipe. One of the $\frac{3}{4}$-in. pipes carries strong acid from the lead tank, and the other ordinary cold water from the mains. The $1\frac{1}{2}$-in. pipe serves to carry the hot mixture to the pot without spatter. This form of pipe requires a minimum of repair, and mixes about 5000 lb. of 75 per cent. acid per hour. The lead tank has a capacity of 18,000 lb. of strong acid.

The product of the plant passes through a scale tank and is delivered to the nitric acid plant, where in winter weather it is mixed with 2 per cent. nitric acid to prevent freezing. The entire product can be delivered as 99·5 per cent. H_2SO_4, but for use in making nitric acid a portion is reduced to 94 per cent. H_2SO_4.

In this plant, using Louisiana brimstone for eighteen months there had been no indications of poisoning, and the converter had not been opened. The temperature of gas entering the converter was kept constantly at 380°, and conversions were regularly 95 to 95·5 per cent. This low temperature means a decided saving in coal, and in wear and tear of the preheater. During six months the average consumption of coal had been 21·8 lb. per 100 lb. of trioxide made. An entrance of gas of 6·5 to 7 per cent. was regularly used. During six months under the above conditions, the average make had been a little more than 7 tons of acid per day, and the average yield on sulphur fed to the burner 93·36 per cent. The plant can make a maximum quantity of 8 tons with a yield of 90 per cent. Comparison of cost sheets showed that by changing raw materials from pyrites to brimstone, the cost of manufacture had been reduced nearly two dollars per ton of 98 per cent. acid. This reduction was due in part to reduced losses from shutdowns for repairs, in part to increased yields, and in part to saving in coal and reduction of the cost of upkeep.

GRILLO PLANTS BURNING PYRITES.

Before 1914 a number of Grillo plants were burning pyrites or zinc blende on the Continent and Overseas, but in this country there was none, nor, indeed, a complete Grillo plant of any kind. In France and Belgium, where the oleum production before the War was very small, there were several small installations at St Gobain and elsewhere. During the War a number of plants, some of them of very large capacity, were erected in both Great Britain and France, by the Simon-Carvés Company. At the Dalton works of the British Dyestuffs Corporation a large installation of twelve units designed to produce 120 tons of 20 per cent. oleum per day, was put up in 1915. At the works of the United Alkali Company at Widnes and St Rollox units each of 20 tons capacity were erected, a similar unit being built for the Cleckheaton Chemical Company. There is also a 15-ton plant in Wales, designed to burn zinc blende, and a 10-ton sulphur-burning unit was erected by the same firm for the Japan Dyestuffs Corporation.

The Paris house of the same firm (*Entreprises Simon Carvés*) also erected plants in the following situations (the capacity is in each case stated in tons of 20 per cent. oleum per day): *Poudrerie Nationale de Saint-Chamas*, 100 tons; Miramas Works, 45 tons; L'Estaque Works of the *Etablissement Kühlmann*, 20 tons (these three were pyrites-burning plants); *Société Royale Asturienne des Mines Aviles*, 40 tons; Pennaroya Works, 20 tons; Tonnay-Charente, 40 tons (these three burnt zinc blende). There was in addition a plant at the *Poudrerie Nationale de Bergerac*, which was to have a capacity of 120 tons, but was dismantled at the time of the Armistice and fitted up again in the Kühlmann works at Loos and La Madeleine. Of the plants built by the Company in France, those which were working during 1922 were situated in the Kühlmann works at Rouen, 20 tons; L'Estaque, 20 tons; Loos, 60 tons; and La Madeleine, 90 tons. All these four works burns Spanish pyrites.[1]

On the plant of the British Dyes Corporation, each unit has a Moritz burner, capable of burning 10 tons of pyrites

[1] Information kindly supplied by the Simon-Carvés Company.

fines per day. This burner has eight shelves and the ore is fed in by a plunger-feeding mechanism, the stroke of the plunger being variable. The central shaft is cooled by forced air draught, and the five upper arms are also cooled by internal air circulation along the arm and back over a dividing feather into the interior of the shaft again. The hottest shelves are the third and fourth, and the burnt ore from the last shelf is quite cold. Admission of air to the shelves is controlled by small slides. The shaft rotates once in about three minutes. In this burner the percentage of sulphur in the cinder can be reduced to 1·5 or 2·0. All the twelve burners are placed in a single burner-house, and several movable platforms, travelling on overhead runways, are fitted for access to any of the furnace doors. The burner works well and does not run too hot. The layout and the working of this portion of the plant are very favourably regarded.

Following the burner, in the plant as first erected, was a dust chamber containing a number of brick-built compartments, through which the gas passed in succession. A brick-lined steel pipe led to this from the burner. Leaving the dust chamber, the gas passed into the bottom section of the first acid wash-tower, constructed with lead, lined with brick, and supplied with acid very much as in a Glover tower. A certain amount of concentration of acid took place here, and the washing process was carried further by passing the gas into a second tower, constructed in the same way as the first, but filled with coke instead of with bricks. Leaving the second tower the gas was drawn through three filters in succession, each being constructed of lead in the usual way, and filled with coke. After passage through a single drying tower of lead, the gas issued to the conversion system by the Roots blower which followed next in order, and was coupled in the ordinary way to a grease-catcher.

The conversion system consisted of two jacketed converters similar to those of the D.E.S. Grillo plants, and two gas-fired preheaters also of somewhat similar design. Each of the four layers of mass in the converters contained about 0·25 per cent. of platinum. The preheaters were required in ordinary operation.

The absorption system comprised five horizontal absorbers

and two absorption towers of the kind described previously in this chapter, with appropriate pumps and coolers.

The working of the purification system of this plant was defective, and after being in operation with a low efficiency for about four years, the plant was closed down. It should be mentioned that the plants in France, in which the purification system was built on a more liberal scale, have operated, and are still operating in a more satisfactory manner.

Modifications have now been carried out on part of the plant of the British Dyestuffs Corporation which have proved very successful. After the burners have been installed a Cottrell dust precipitator capable of taking the gas from two burners in each of the two halves into which it is divided. The negative electrodes are steel rods and the positive electrodes steel plates stiffened with angle iron. A voltage of about 60,000 is employed. The temperature throughout the precipator is much above that at which sludge can form, and the perfectly dry dust falls into shutes from the ends of which it is removed by a chain-extractor. All but a few per cent. of the dust from the burners (which represents on the whole about 3 per cent. of the weight of the cinder) is thus removed.

The gas from two burners (*i.e.*, from each half of the precipitator) is then led to two acid wash-towers in series, as on the old unit, and passes from the second of these towers to a Cottrell mist precipitator. This consists of two leaden cylinders containing a number of lead tubes through the axis of which the negative electrodes pass. All but a few per cent. of the mist particles are then taken out. Next in order are two coke filters in series, of augmented size, filled with coke which has been carefully sized and washed.

In order to reduce the mist still further, and to absorb such impurities as hydrochloric acid, the gas from the precipitators is taken through two towers in series, down which a flow of liquor (initially containing about 0·2 per cent. of sodium hydroxide) is maintained by pumps. These two towers are the same in construction as the acid wash-towers, whose function they formerly fulfilled. Returning from them the gas is drawn through a washer designed on the lines of a Livesey gas-washer. On entering the washer the gas is sprayed in the pipe with fresh alkaline liquor, and then receives a very

thorough scrubbing by bubbling through the alkaline liquid under numerous series of serrated edges. The liquor from this washer is removed by overflow and is supplied to the circulation tanks of the alkaline wash-towers. To remove spray from the gas a "stripper" is provided in the form of another coke-filled leaden filter, and after making its way through two drying towers in series, the gas is ready for conversion. To the conversion system heat-exchangers have been added.

This system is an interesting one, combining as it does the features of acid cooling and washing, electrical precipitation of both dust and mist, and scrubbing with alkaline liquid. It is giving excellent results.[1]

In another unit erected in the North, shortly after the Dalton plant was completed, two Moritz burners were fitted, so that the capacity of the plant was about 20 tons of 20 per cent. oleum. The purification system was different from that of the first plant to be described. After the two acid wash-towers, was installed a battery of ten filters, made of lead and packed with quartz, and similar in construction and arrangement to the filters of the Tentelew plant. After these came two brick-lined cast-iron towers packed with acid-proof rings, down which a liquor (made up to contain 0·5 per cent. of sodium hydroxide) was circulated by Marcus Allen pumps. Then followed a "stripper," three cast-iron, brick-lined drying towers, and an acid spray-catcher, also of cast-iron, with connections of the same metal. The gas was then drawn through an equaliser into the blower.

The introduction of washing with bisulphite solution in packed towers, and the substitution of the small Tentelew dust-catching filters for the ordinary large coke-filled vessels did not prove to be a success, and the plant ran only for a short time.

[1] For this ingenious and very adequate transformation of the plant, Mr S. Robson and the staff of the British Dyestuffs Corporation are responsible. Acknowledgment is due to the Corporation for permitting the publication of these facts.

CHAPTER IX

THE TENTELEW PROCESS

THE process of the Tentelew Chemical Company was worked out by Eschellmann and Harmuth, respectively technical manager and chief engineer of the firm, and the patents were taken out in the name of the three parties. Until 1886 all the fuming sulphuric acid consumed in Russia for the manufacture of lubricating oils from crude naphtha had been imported from abroad at the abnormally high price paid to the Bohemian firm of Starck. In this year the work of the Tentelew Company began. Many experiments were made; one apparatus was replaced by another, and in the course of years many processes were tried out on a large scale before a satisfactory and economical one was found. In the end success was attained, and the consequent fall in the price of fuming acid in Russia led to a great extension of the Russian petroleum industry.

It has been stated by the firm [1] that the first acid produced by them (100 per cent. H_2SO_4) was sold as far back as 1886, and that the main features of the process were used by them from 1894 onwards. The inventions were first announced in 1901, when the Company applied for foreign patents in most countries.

These applications were vigorously contested by the *Badische*, but the opposition failed. The German Patent Office decided in 1905 that the Tentelew method of purification, for which a patent had been sought in 1901, was actually the result of original inventive action, and in spite of the *Badische's* representations a patent was granted in 1907. It was acknowledged that specially valuable advantages were secured by the *successive* removal of sulphuric acid and of chlorine compounds from the burner-gas.

[1] Communication to Lunge.

The Tentelew purifying process was characterised by dry filtration and separation of the fog before washing, and by the application of *alkali* for purifying the gases, thus introducing a chemical purification, whereas the *Badische* process of purifying by means of sulphuric acid employed mechanical and physical means. The great advantage of the Tentelew process was proved by the fact that the same contact-mass had been working in their first large contact-apparatus for nine years, and still yielded a 97 per cent. conversion.

The following comparison shows the main differences between the Tentelew purification process and that of the *Badische* at the time when this question had been fought out:—

Badische.	*Tentelew.*
1. Addition of aqueous vapour t the hot burner-gases.	1. No such addition is made.
2. Cooling.	2. Cooling.
3. No filtration.	3. Dry filtration and separation of sulphuric-acid fog.
4. Washing with sulphuric acid fc the purpose of removing the sulphuric-acid fog.	4. No such operation.
5. No treatment with alkali.	5. Washing with alkaline liquor.

During the first year of working efforts were mainly directed to producing cheaper fuming acid, but, later, attention was turned to the production of ordinary acid, the object in view being to dispense with the lead-chamber plants. The *Badische*, their competitors, were the first to do this: the Tentelew Company followed suit. Finally, the antagonism between the two was resolved by an agreement by which the interests and experience of the two firms was shared. The *Badische* is now involved with the other large German firm in the *Interessengemeinschaft*, but the close relations with the Tentelew Company are still understood to hold.

By 1911 the process had been sold to Nobel Brothers at Baku (2 sets), Steaua Romana Company at Gampina (Roumania); Merrimac Chemical Company (at Boston, 2 sets); General Chemical Company, New York; Weiler-ter Meer at Uerdingen (2 sets); Dynamite Nobel at Hamburg (3 sets); Kopparbergs A. B., at Falun; Oehlrich & Company at Riga; Uschkoff & Company at Kasan. At the end of 1911[1] 24 sets

[1] *Chem. Zeit.*, 1912, 218.

of the Tentelew apparatus for 4000 tons of trioxide each were at work in Russia, Germany, Roumania, Sweden, America, and Japan.

Tentelew plant was erected by Nobel's Explosives Company shortly before the War, and the Mannheim plant which they had formerly worked was superseded. This firm, the chief constituent company of Nobel Industries, Limited, has now four units of Tentelew plant of modern design at their Ardeer works. During the War a large Tentelew plant of six units was erected by this firm in the cordite factory at Pembrey, which they were managing for the Department of Explosives Supply. A similar plant of two units was also erected at the Royal Naval Cordite Factory at Holton Heath, and is still in operation.

In Italy the oleum plants built during the War were mostly of the Tentelew design. Two units were installed at Cengio by the *Societa Italiana Prodotti Explodenti*, and three more were built by the *Union Concini*, two at Bovisa and one at Vicenza.[1] There are also plants in Japan, in the Baeyer works at Ludwigshafen, and at Schlebusch.

The following is a list of the Tentelew patents in this country, the United States, France, Germany, Belgium, and Italy.

(*a*) *Contact Process.*—B. Ps. 11969 of 1902, 20952 of 1904, 23419 of 1909; U.S. Ps. 792205 of 1905, 937148; Fr. Ps. 321275 of 1902, 3778 of 1904 (addition), 407914 of 1909; Belg. Ps. 163469 of 1902, 179782 of 1904, 219865 of 1909; Ger. Ps. 178762 of 1904, 227095 of 1909; It. P. 139, vol. cliii., p. 189, vol. cxcvi., p. 314, vol. lxxxvi. (*b*) *Gas Purification*—B. P. 12213 of 1907; Fr. P. 379565 of 1907, 194176, 230585 of 1910; Belg. P. 199923 of 1907; It. P. 211 (vol. cclxviii.) of 1907. (*c*) *Absorption Apparatus*—B. P. 22095 of 1907; Fr. P. 382081 of 1907; Ger. P. 211999 of 1907; It. P. 187 (vol. cclxi.). (*d*) *Burner-gas Cooler*—B. P. 14670 of 1911; U.S. P. 1078841 of 1913.

The distinctive features of the Tentelew system are found in the purification and conversion systems. Either pyrites or sulphur can be used. The burner-gas is cooled to the temperature of filtration by passage into a leaden gas-cooler of special design surrounded with water, and is then freed

[1] Cantimorri, *Giorn. Chim. Ind.*, ed. App., 1923, 10, 66.

of the greater part of the residual acid and solid matter by passing through quartz filters adapted for cleaning out when necessary. It is then washed in a bubbling tower with a number of compartments, into which is fed at the top a dilute solution of sodium hydrate. After being deprived of spray, dried, and passed through filters to remove mechanically carried particles of drying acid, the purified gas is forced, by means of a blower, which on modern plants is of the turbine type, through the preheater and converter. Platinised asbestos is used as contact-mass, and the comparatively high concentration of platinum in conjunction with the use of an efficient type of tubular heat exchanger makes it possible in some cases to run without the use of fuel for heating the gas to the temperature of reaction. The converter has special features which have already been indicated. The converted gas is cooled in tubular coolers, and passes to an absorption system consisting of several absorbers of the bubbling type, the arrangement of which may be varied to meet the requirements of the plant.

No metal but lead is in contact with unpurified burner-gas. The cooling, washing, and drying towers are usually cast in flanged annular sections. Each section is suspended from a steel supporting structure by means of a collar passing round it, and tie-bolts attached to the collar. In this way any section is relieved of the main part of the weight of those above it, and the tendency to collapse is minimised.

Contrasting the plant with the less developed Grillo and Mannheim systems, which, with one or two exceptions, are the only others adopted in this country, it is seen to have a more efficient purification system, simpler and better heat-regeneration apparatus, and on the whole a greater flexibility in operation. On account of the use of a gas-washing tower, of a comparatively closely packed converter and of bubbling absorbers, the pressure at which the gas is drawn or forced through the plant is high, and a greater expenditure of power is therefore necessary.

The ensuing descriptive notes (Plant A) apply in general to Tentelew plant of modern design, but to no particular installation. Plant B is older, and represents an earlier stage of development. In the first case the unit has a capacity of about 11 tons of trioxide per day, in the

second it is about 5 tons. Plant A burns pyrites, Plant B sulphur.

TENTELEW PLANT (A).

In plants of this type pyrites is burnt in rotating mechanical burners, and has consequently to be crushed and screened first of all by passage through jaw crushers and rotary screens. The crushed ore, sized to about $\frac{3}{8}$ in. and under, may be carried to the burners on an overhead runway and tipped into the feed hoppers. A semi-automatic weighing machine is often built into the runway.

The order in which the various elements of the unit are connected with one another can be seen from the illustration of Fig. 104, which is diagrammatic only. In a modern installation the plant is set out as far as possible in one straight line.

The Pyrites Burners.—To each unit two mechanical furnaces may be fitted, each having a nominal capacity of 5 tons of pyrites a day, and a third is sometimes provided as a standby. These burners are in some cases of the Lurgi type, and are similar in general construction, although not in detail, to Herreshof furnaces. Each consists of an upright cylindrical steel shell about 11 ft. 6 in. in diameter by about 15 ft. high, and inside this shell is a brick structure consisting of seven or eight circular hearths, one above another. Through the centre of these hearths passes a vertical shaft which is kept cool by air convection, and at each level, cast-iron rakes are fitted into the shaft by a locking device. As the shaft rotates, the rakes revolve and stir the whole surface of the charge on each shelf. The teeth of the rakes are set to impel the charge inwards and outwards on alternate shelves. In each shelf are two holes so arranged that the ore is worked to the outside on one shelf and then falls through a pair of holes on to the shelf below. Here the set of the teeth of the rakes causes it to pass towards the centre, where are two holes delivering it to the next tray, and so on. The ore is supplied at the top of the furnace from a hopper, provided with a worm feed driven from the main shaft. The passage of air between the revolving shaft and the bottom tray is prevented by the provision of a lute packed with sand, burnt pyrites, or fine quartz, in the usual way. The usual rate of rotation of the shaft and arms is about half a revolution

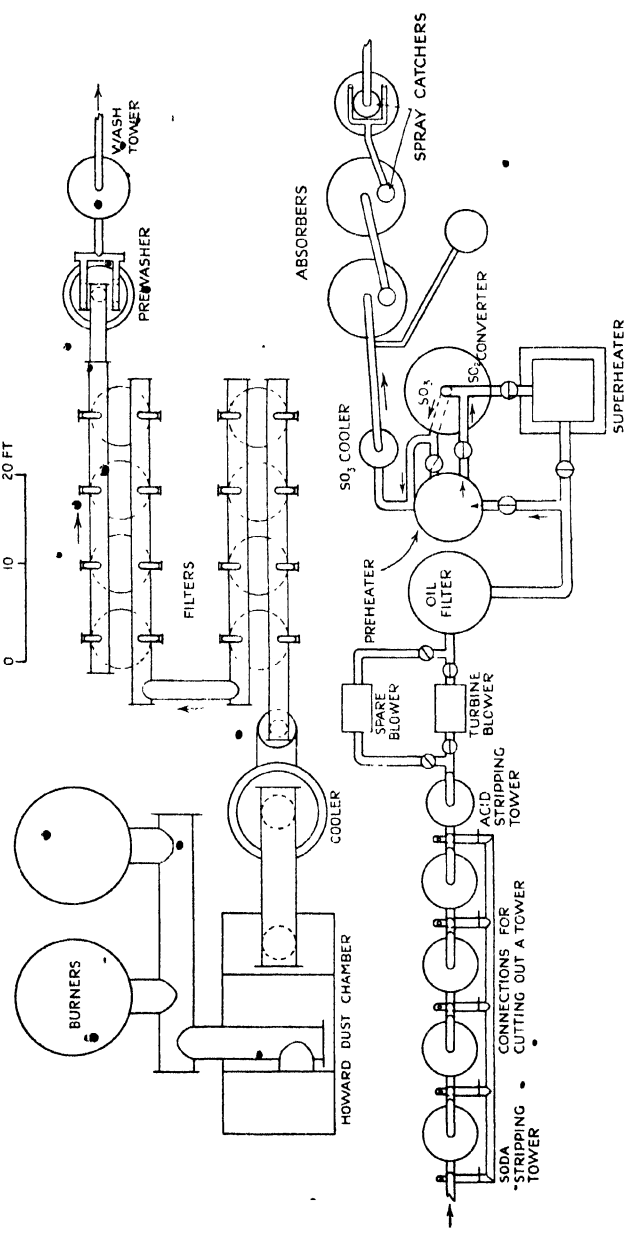


FIG. 104.—Tentelew Plant (A). Diagram of Gas-Connections.

in a minute. For each group of two furnaces, a motor drives a main shaft to which pinions are attached bearing on the horizontal bevel wheels of the furnace shafts. A suitable reduction of the speed of the motor is obtained by reducing-gear. The burnt ore drops out of a hole in the bottom tray into a closed iron box running on rails. Doors are provided to give access to each shelf; there are also inspection-plugs and small ports with sliding shutters by which the entrance of air to the trays can be controlled.

The temperature maintained in the three top shelves is round about 750° with pyrites containing from 48 to 50 per cent. of sulphur. The lower shelves are not so hot. If the full amount of 5 tons is burnt each day, the temperature may become excessive, and as a result, slag is apt to form. This is most likely to occur on the first shelf, but No. 3 is usually the hottest, and here the heat is most likely to damage the arms, by causing them to bend upwards and finally to break. When an arm is broken the access-doors are opened and the pieces removed, the slag is taken out from the shelf and a new arm, preferably fitted previously to a similar shaft, is inserted. If the pyrites is too fine, slagging will occur. The amount of residual sulphur in the cinder depends, of course, largely on the nature of the ore, but a final content of 2 per cent. is not unusual.

The gas from the burners issues at the top into a cast-iron main about 3 ft. 6 in. in diameter, lined throughout with 2 in. of fire-brick and provided with dust chutes and scrapers for cleaning. Through this main the gas passes to a dust chamber of the Howard type. The chamber is built of brick, bound with steel channels and tie-rods, and is divided by a longitudinal wall so that one half can be cleaned out while the gas is passing through the other. To effect these changes a number of cone valves operated by geared winches are fitted to the inlet and outlet parts of the chambers. Each chamber contains a large number of steel sheets, all placed horizontally, from 3 in. to 6 in. apart. The cleaning of a dust chamber, of the outlet pipes from the burners, and of the gas-main is carried out at regular intervals, the length of which is ascertained by experience.

Purification System.

The Burner-gas Cooler.—Leaving the dust chamber, the gas passes into another cast-iron main about 3 ft. wide, lined with brick, from which also the dust has to be removed at intervals, and then enters the burner-gas cooler—one of the special features of the Tentelew design. This vessel is about 22 ft. high in all, and consists of a cylinder made up of five sections of cast-lead rather more than 1 in. thick and about 8 ft. in diameter, which are built up on a strong cast-iron ring about 10 ft. in diameter standing on four cast-iron pedestals. The construction of this cooler can be made clear from the description given in the patent of 1910, which differs from actual present practice in certain respects, but is nevertheless essentially applicable. The cooling of hot gases to the temperature necessary for purification, in one operation, is a matter of great difficulty, for leaden tubular coolers are apt to be destroyed rapidly by the action of hot acid and the formation on them of hot crusts of flue dust. These drawbacks are avoided by using hollow plates, as shown in Fig. 105. The left side of the elevation is a vertical cross-section on the plane CD; the right side is an elevation at right angles to the first. The upper half of the plan is a horizontal cross-section on the plane AB.

The apparatus consists of a preliminary cooling section *b*, into which the gas enters through the T-piece *d*, attached to the main; the main cooling space *a* of four sections; an outlet chamber *f*, and a trough *g*, where the condensed acid forms a lute for the whole cooler. The inlet pipe passes into the dome of the cooler through a loosely packed joint. There is therefore no rigid connection, and expansion of the leaden dome is not restricted. Each of the rings *h*, which form the cooling chamber proper, is cast with three parallel hollow diaphragms, *i*, *i*, which, in plan, form complete chords of a circle. The upper edges of these diaphragms are inclined downwards to the centre, so that overheating cannot be caused by air or steam being trapped in contact with the hot walls. Stays *k*, *k* keep the diaphragms in place, and the weight is borne on bosses which are placed between each pair. Round the whole cooler is a water jacket of steel plate *l*; and into this water enters at *m*. The water enters and leaves the

24-in. main the gas is carried to the top of the filter-box by a 6-in. lead pipe, connection with the main being made (on both inlet and outlet) by an inverted U-bend with lutes, so that any filter can be cut out from the others for cleaning.

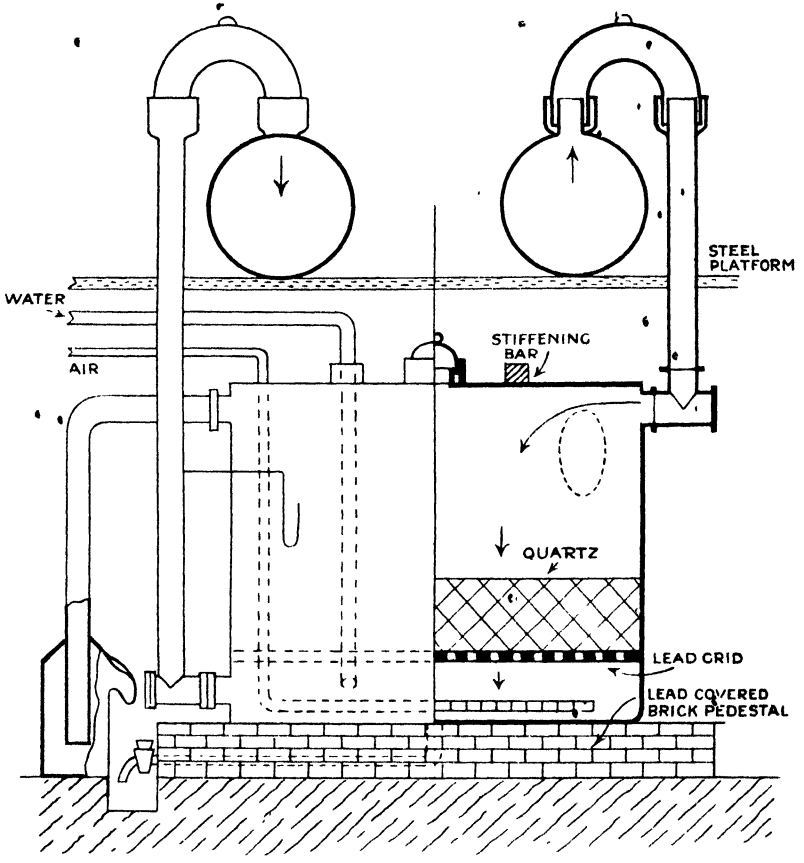


FIG. 107.—Tentelew Filter.

A platform is provided at a suitable height to facilitate inserting and withdrawing these bends. The packing consists of quartz sized to about ½ in., and this is packed on to a lead grid, suitably strengthened to take the load. Each filter contains 1½ tons of crushed and sized quartz.

Water can be supplied to the filter through a 3-in. pipe, and compressed air can also be blown in by means of a distributing

pipe below the grid. The outlet pipe for water leaves the filter at the top and delivers to the drain through a lute which prevents air being drawn in when the filter is in operation. The whole apparatus may be placed on a brick pedestal covered with lead, and the lead covering may be continued between the pedestals and inclined so that waste can run easily to the drain.

Much dust may be caught in these filters, and when any one of them is found to offer a high resistance to the gas, on account of the passage through the quartz having been obstructed, it is cleaned by flushing out with water, from the bottom upwards. The frequency of cleaning varies with the character of the ore being burnt, but one or more filters may be cleaned each shift, or at least three each day.

Gas Scrubbers.—From the filters a 20-in. main leads to the prewasher (Fig. 108). This is a scrubber placed before the wash-tower and containing a single bell placed inside a cylindrical lead casting of about 6 ft. diameter, 3 ft. depth, and 1 in. thickness. The gas enters through the cast-lead cover into another concentric cylinder, the lower end of which is belled-out, and makes its way up through the liquid after passing through the serrations at the edge of the bell, or through four rows of holes in the rim, about $\frac{1}{2}$ in. in diameter. Four 6-in. outlet pipes collect the gas from the annular space between the shell of the washer and the bell. Water connection is provided and there is also compressed-air connection to two perforated half-coils which lie on the bottom and can be used for air stirring. The prewasher is surrounded with a steel water-jacket and stands in a large cast-iron tray.

The wash-tower (Fig. 109), into the bottom of which the gas leaving the prewasher is drawn, comprises five or more superimposed cylindrical lead castings, each about 6 ft. in diameter and 3 ft. deep, all burnt together. In each section is a mushroom-shaped bubbling plate with circular rows of perforations, or with serrated edges and perforations as well. In either case the plate is very firmly fastened down to avoid vibration. Dilute sodium hydroxide solution of about 1 per cent. is supplied to the top of the tower from a storage tank, and overflows from one section to another until it reaches the bottom. It is then passed into the prewasher through the

lower of the two side pipes shown in Fig. 108, and from there overflows through a lute to the drain. The waste liquor consists mainly of dilute sulphuric acid with sulphur dioxide in solution. Provision is also made, as the sketch shows, for

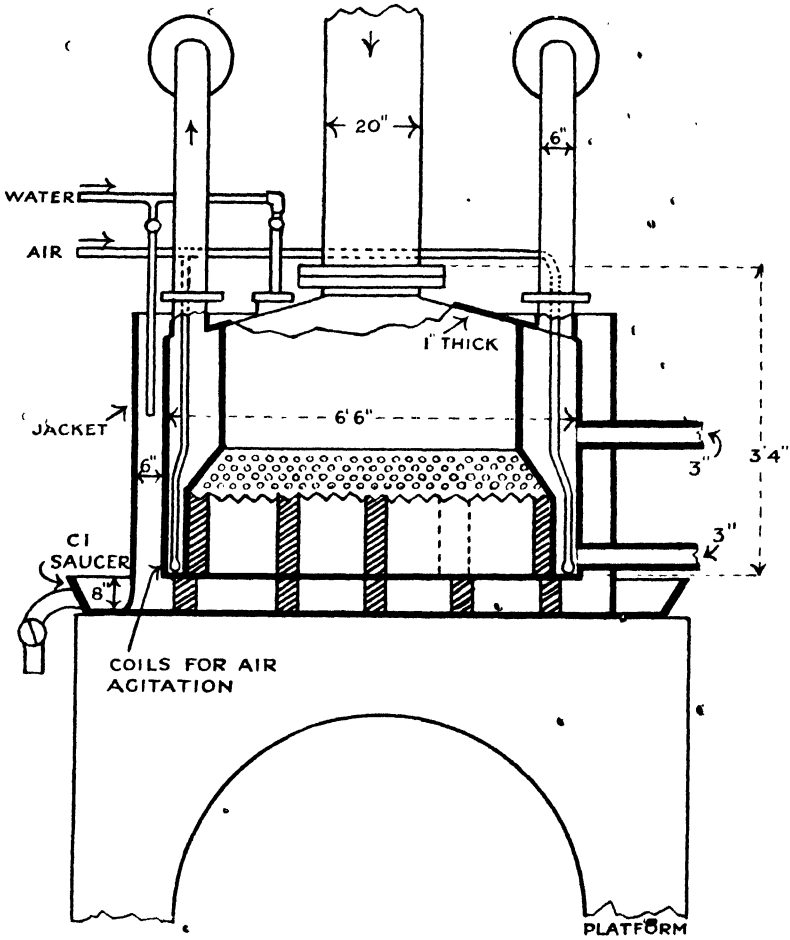


FIG. 108.—Pre-washer—Sectional Sketch.

draining the liquid completely away from any section and so cleaning out the tower—an operation which is performed at frequent regular intervals.

To supply the tower and prewasher with the dilute alkaline solution, from one to two kilos of sodium hydroxide is required

every twenty-four hours, the quantity used being increased if the arsenic or chlorine content in the gas to be dealt with is found or expected to rise. The completeness of the purification is controlled by frequent tests of the arsenic content of the liquid from each section of the washing tower, and the gas leaving the tower is submitted to the continuous test by bubbling through water, the solution being examined

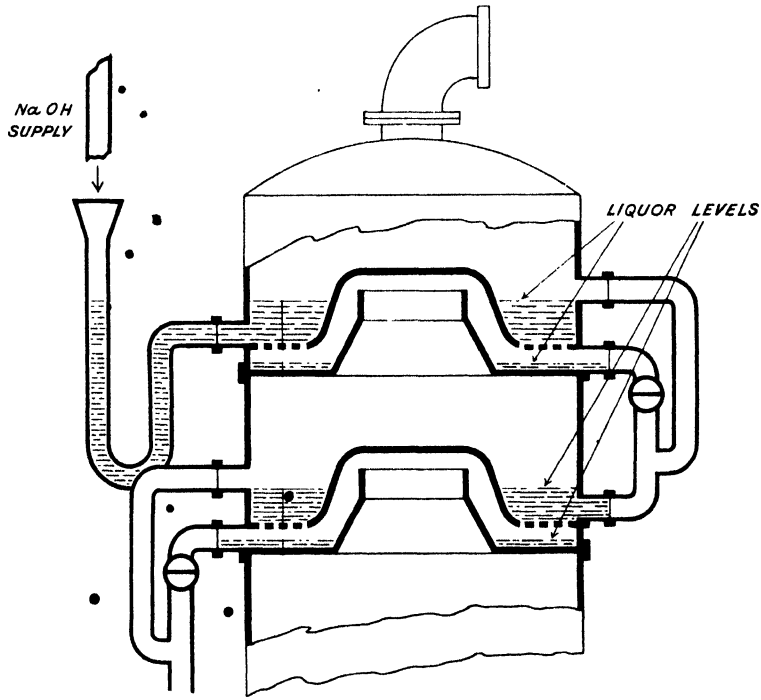


FIG. 109.—Sectional Sketch of Wash-Tower.

afterwards for arsenic. This method of purification is very satisfactory for pyrites burner-gases in ordinary circumstances, when carefully controlled by those who have had experience of it. No trouble is experienced from hydrochloric acid poisoning, and the elimination of arsenic, in nearly all circumstances, is very complete.

Drying Towers.—The purified gas, which now needs only drying, passes next to the drying towers—four in number. Each consists of three sections 5 ft. in diameter and 6 ft. 6 in.

in height, made of heavy sheet-lead and burnt together with a domed cover, and is built up on brickwork about 5 feet above the floor level in order to allow of an acid lute in the pipe through which the circulating acid flows down to the lower tank. Each section of the tower is supported by a cast-iron ring suspended from four cast-iron columns, which are bolted to an iron base-plate. The lower part of the tower is packed with acid-proof bricks to a height of about 3 ft., and above this is placed about 15 ft. of hard graded coke. The first tower of the set of four is not supplied with acid, and is used to filter out any spray or mist which may have been carried over from the washing system ("soda stripping tower"—S.S.T.). Through the other three, sulphuric acid is circulated by means of centrifugal pumps, being spread over the upper surface of the coke by earthenware distributing-plates. The strongest acid circulates in No. 3 and the weakest in No. 1, provision being made for transference of acid from one circulation to another through overflow pipes, as drawn in the diagram of Fig. 110, The direction of the gas-current is upwards in each case.

The strength of the acid used for drying, and the extent to which it is diluted in use, vary with circumstances. Care is always taken that arsenic is not introduced from it into the gas leaving this series of towers. In some cases the drying acid is made specially in an auxiliary absorber, and after use for drying is returned as feed to it. In this way there can be no arsenic contamination so long as the washing system operates properly. As water is constantly being carried from the drying tower to the auxiliary absorber, more acid may be made in this system than the drying requires, and an excess of either weak or revivified acid remains for other purposes. The connections may be as shown in diagrammatic form in Fig. 110. Acid from the absorber of about 98 per cent. is delivered to the covered supply tank of the third drying tower and is pumped to the top. It flows from the bottom of the tower through an overflow box, in which is a perforated lead plate to retain stray coke, and runs into the tank. The overflow from this tank runs into the next, and so on to the third, in which the acid may have fallen in strength to about 80 per cent. Overflowing from the last tower supply tank, the weak acid is raised to a tank which supplies the auxiliary absorber.

It is necessary from time to time to clear the drying towers from sludge which is apt to deposit in them; especially if the acid, as sometimes has been the case, is that recovered from the spent acid mixture of nitration processes. To do this, it is very convenient to be able to detach one tower from the rest without much interruption of the plant, and connections designed to facilitate this are provided. An additional gas-main runs along the towers, and is connected with the entrance pipes by short lengths into which blind flanges or "spades" are inserted. With the insertion of suitable "spades" in the

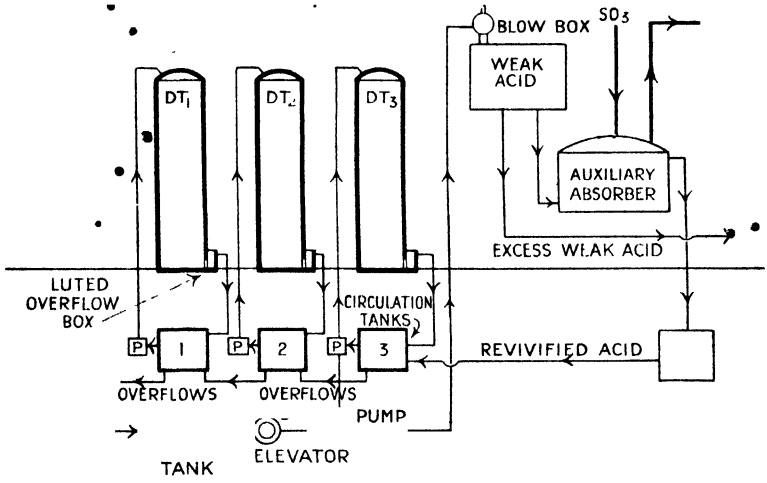


FIG. 110.—Tentelew Plant—Acid-Connections to Drying-Towers.

entrance pipes, and the withdrawal of two similar ones from the short pipes, any towers can be cut out without interrupting the gas circulation. The washing out can be done very thoroughly by filling the tower with water, but the heat of reaction between the water and the acid diffused in the coke is considerable, and care is necessary.

In the diagram of Fig. 104 five towers are shown. The last is the acid-stripping tower, the function of which is to remove any acid spray mechanically carried over from the drying towers. It is constructed and fitted in much the same way as the drying towers, but is often smaller—about 5 ft. wide and 10 ft. high, and no acid, of course, is circulated through it. The first is the "soda-stripping" tower.

On leaving this series of towers the gas passes directly to the blower, having come into contact with no metal other than lead since leaving the dust chambers. The suction at the entrance to the blower represents the total resistance of that part of the plant which has so far been described, and amounts to about 10 cm. of mercury. Of this resistance the washing tower is responsible for from 5 to 6 cm., and the drying and stripping towers for the greater part of the remainder. These figures, of course, are only rough indications, and must vary with the charge to the burners and the gas concentration.

The Conversion System.

The Blower.—Other types of gas-pump have been superseded by the turbine blower, which has the great advantage of working without the pulsations which are so injurious to leaden plant. The Parsons' blower often used is a four-stage machine, run by a motor of about 75 h.p. and about 1000 r.p.m. To obtain the necessary speed the impeller is geared up to 4000 or 5000 r.p.m. by double helical gearing with pressure oil circulation. Motor, gearing, and blower are mounted on the same bedplate. The pressure at the delivery is 12 or 13 cm. of mercury when from 10 to 11 tons of trioxide are made each day, the gas containing from 6 to 7 per cent. of dioxide.

After the blower an oil-filter is provided to remove any oil which may have been carried over. This consists of a steel cylinder about 9 ft. in diameter and of slightly greater length, packed with coke on a perforated plate. It is found, however, that turbine blowers of the type mentioned have the additional advantage of passing little or no oil. From this oil-filter, in ordinary running, the gas passes to the "preheater," and converter.

The Heat Exchanger (or "preheater") is a cylindrical apparatus, the shell of which is about 14 ft. long, and 6 ft. 6 in. in diameter. It contains two tube plates, and in these are set from 300 to 350 tubes about 13 ft. long and 2 in. in diameter. The hot gas from the converter passes through these tubes, and the cold gas round them. A similar apparatus is described in the Tentelew patents, and is illustrated in Fig. 25. The cold gas enters at the bottom, passes upwards

over the tubes, and leaves at the top below the upper tube plate. The hot gas from the converter enters the heat exchanger at the bottom, and passes upwards through a large pipe fixed centrally into both plates, and then downwards through the numerous smaller tubes. The heat exchange is therefore carried out in counter-current. In operation it is found that the preheating thus obtained, in addition to that for which the converter itself is responsible, is more than sufficient. A by-pass valve is therefore fitted (shown in Fig. 25 below the heat exchanger), by means of which the gas may be transferred to the extent required, without passing through the pipes at all. A manhole is fitted on the top to give access to the tubes, and a drain is provided in connection with the bottom to remove any acid which may condense.

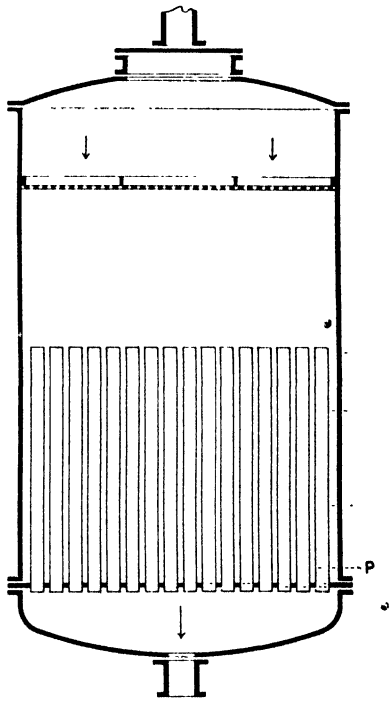


FIG. 111.—Tentelew Converter.

The Converter has already been mentioned in the section dealing with converters, and it has been noticed that its special feature lies in the preheating and temperature-regulation which are obtained simultaneously by the free circulation of the gas round the tubes containing the contact-mass. In the type of plant now being discussed, the converter is of the type illustrated in Fig. 25 and is represented in the sketch of Fig. 111. The gas enters at the top, through a flange fixed to the removable cover, and passes downwards through a distributing diaphragm formed by light, perforated cast-iron plates on which asbestos is placed. The centre plate of this diaphragm—which serves the double purpose of filtering out coarse dust and acting as a gas distributor—is removable, in order to give access to the contact-tubes. Below this is a

free space which amounts to a considerable fraction of the whole space of the converter, and is proportionately greater than that shown in Fig. 25. The converter is about 16 ft. high and 9 ft. in diameter. In a heavy tube plate at the bottom are set the contact-tubes—5 in. in external diameter, about 6 ft. 9 in. long, and 200 in number. These tubes are held only by their lower ends. Each tube contains from 55 to 60 malleable cast-iron discs on which the contact-mass is placed. Fig. 112 shows these discs. The top of the pin of each disc fits into the hole in the base of the one above. A regular series of shelves is thus provided in the tubes, and on each shelf a fixed weight of mass is placed, but a few trays at the top and bottom of each tube are filled with unplatinised asbestos only. Pyrometers are fitted into the converter near the entrance to the tubes and in other suitable positions.

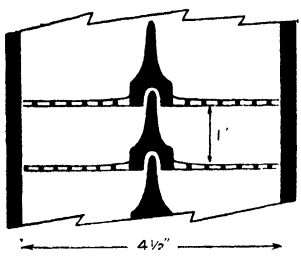


FIG. 112.

On each plate is distributed about 13 gm. of platinised asbestos which has been carefully teased out. The percentage of the platinum on the dry contact-mass is from 7½ to 9, and each converter contains from 24 to 26 lbs. of metallic platinum.

The Superheater is similar to that represented in Fig. 113, and consists of a cast-steel header about 5 ft. square and 1 ft. 6 in. deep. Inside this header is a tube-plate into which are expanded 120 steel tubes of 1¼-in. bore. Round each of these tubes is a wider one of about 3½-in. bore and about 8 ft. long. These wider tubes are expanded into the base of the header. The whole superheater is set in brickwork and fired by a coal fire. The cool gas passes down the inner tubes and up the concentric annular spaces. The inner and outer tubes are kept in this concentric position by light "spider" irons. The inlet and outlet in this element, as in the other elements of the conversion system, are of 10-in. bore.

Operation of the Conversion System.—When the plant is being put in operation for the first time, or after cooling down, air is drawn in by the blower at some point in the purification system—frequently at the lutes of the coolers—and is forced

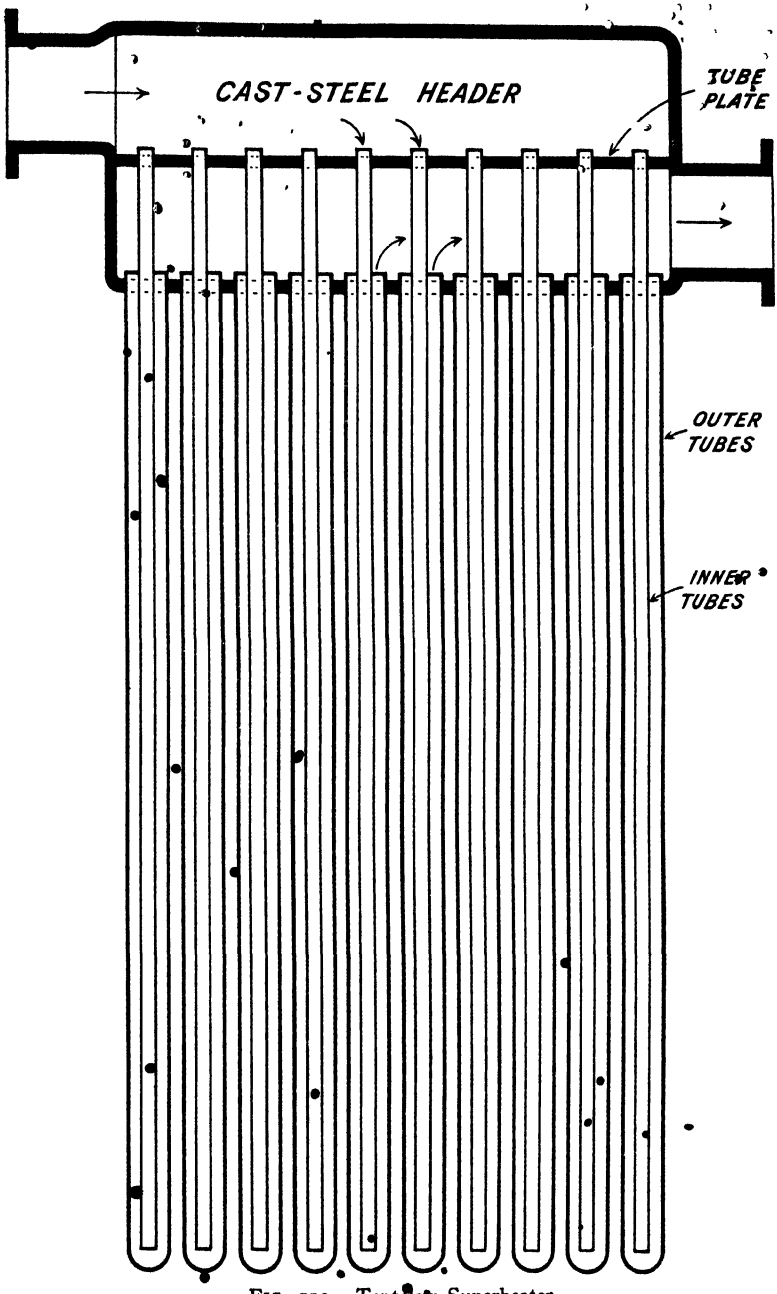


FIG. 113.—Tentelew Superheater.

through the superheater into the converter. By means of valves worked from the floor-level with long spindles, the preheater may be cut out during this operation, and the condensation of acid in it at low temperatures avoided. The necessary connections are indicated in Fig. 104. The temperature of the converter and the contact-mass slowly rises, and when it is high enough, the air is replaced by gas-mixture from the purification system, and conversion should begin immediately. The temperature to which the converter must be heated initially may vary considerably, but 350° has often been attained before a successful start. As conversion reaches its full strength, the superheater can be cut out and the preheater used instead, and finally, if other circumstances are satisfactory, the preheater alone remains in use.

Both converter and "preheater" are very thoroughly lagged, as are the connecting pipes. It has already been pointed out that regenerative running is largely dependent on this, and also that it is the easier, the higher the gas concentration. A percentage of sulphur dioxide of 6·5 to 7·5 is considered suitable under ordinary conditions, and for such a mixture it is sufficient to preheat the gas to from 200° to 220° only, in order to secure the best possible conversion. The "preheater" is frequently more than capable of this, and the regulation of the amount of heat exchange is performed by means of the by-pass regulator valve on the pipe admitting the hot gas. About the middle of one of the contact-tubes, the temperature of the mass will be 470° to 480° and the gas issuing from the converter will be at 400° to 420°. Using a 6·5 per cent. gas mixture, the conversion should be 97 or 98 per cent., and with one of 7·5 per cent. conversion may be 1 or 2 per cent. lower, the net production of trioxide remaining about 11 tons.

The Converter-gas Cooler.—On leaving the converting and preheating apparatus, the gas is led to a tubular air-cooler in which its temperature is reduced to that favourable to good absorption. This consists of two cast-steel headers into which are expanded about sixty mild steel tubes of about 2 in. external diameter, and 12 ft. long. From this cooler the gas passes immediately to the absorption system.

The Absorption System.

Absorption is carried out in three absorbers. The first two into which the gas enters are shown diagrammatically in Fig. 114. They are of mild steel plate and are about 8 ft. in diameter and 5 ft. 6 in. in depth. Each is surrounded by a steel water-jacket, and contains a perforated cast-iron bell about

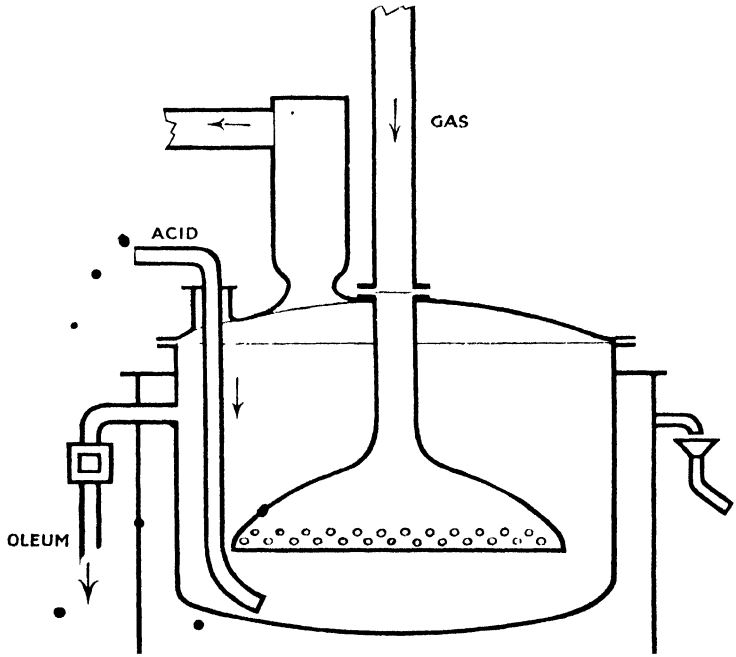


FIG. 114.—Diagram of Tentelew Absorber.

6 ft. 6 in. in diameter and rather more than 1 ft. deep. There is also a cast-steel dip-pipe by which the feed acid is conducted to the bottom of the absorber. The gas enters centrally into the bell and is blown through the perforations into the acid above, and sometimes leaves the absorber through a short wide pipe which is designed to retain spray generated by the bubbling. The finished acid flows away through a lateral outlet-pipe passing through the water-jacket.

The single final absorber, in which is treated the gas which has passed through the other two, is similar in principle, but

instead of containing one large bell it has four smaller ones, all connected in parallel to the inlet pipe. It is deeper (about 7 ft.) and narrower (about 6 ft. 6 in.). In this case also, the outlet pipe (which here is placed centrally) may have a wide spray-catching chamber attached.

In addition to these three elements there may be also an "auxiliary absorber" in which the drying-tower acid can be strengthened, so that the risk of contamination of the mass by impurities from the drying acid can be avoided. This vessel is usually somewhat smaller than the other three and contains a single bell. It is otherwise of the same type. Gas is supplied to it by a 3-in. or 4-in. branch pipe leaving the main just after the converter-gas cooler.

The absorption system may be operated in several ways. All three vessels are frequently connected in series. Feed acid is often allowed to flow into the last of the three (No. 3), the overflow from No. 3 passes into No. 2, and that from No. 2 into No. 1 by gravitation. Oleum runs away from No. 1. This arrangement has been discussed in the chapter on Absorption, and has been seen to have certain disadvantages. Another method is to provide each absorber with a separate feed acid supply, while maintaining the series connection. In this way the strength of the acid in each reservoir can be adjusted independently. More supervision is thus required, but the flexibility is greatly increased, and any strength of feed acid can be used. It would appear at first sight that Nos. 1 and 2 could be operated in parallel to produce 20 per cent. oleum, and No. 3—receiving the gas from both the other two—could be maintained at 98 per cent. If separate feeds were made to each absorber the arrangement would no doubt be a good one, and acids of intermediate strength would be avoided; but there is some difficulty in running absorbers of this type in parallel, on account of the difficulty of exactly equalising the gas-resistances, so that one tends to take an excess of gas at the expense of the other.

Control and Efficiency.—The operation of the plant is controlled by tests at regular intervals for (1) percentage conversion, by estimation of sulphur dioxide entering and leaving the converter; (2) arsenic, by bubbling the gas leaving the wash tower through water, and examining the liquid (see p. 72);

(3) also for arsenic, by testing the solution from each tray of the wash tower; and by other tests as may be thought advisable. In addition, records are made of the pyrometer readings at the converter and in the dust chambers, and the strengths of the absorbing acids are frequently checked with the hydrometer, or by some other rapid method of testing. The sulphur in the burnt ore is often estimated daily.

Efficiency.—In the Tentelew process the losses in operation are due, firstly to the sulphur left in the burnt ore, and secondly to the loss of acid in the filters and washing apparatus. When burning down to 2 per cent. of sulphur in the cinder the overall efficiency of the plant may be 87 or 88 per cent. The loss in conversion is small.

In the published records[1] the Tentelew plant at Pembrey is reported to have worked, during the first six months of 1918, with a mean overall efficiency of 84·2, the highest figure reached for any one month being 86·2 per cent. For the second month of this period the following figures may be quoted.[2]

Pyrites charged (48 per cent. S), 119·8 tons. Equivalent SO_3 = 299·5 tons.
Feed acid charged—
Absorption, 349 tons (92 per cent.) } „ SO_3 = 262·3
Drying, 182·8 tons (90·5 per cent.) }
Acid produced—
Oleum, 604·3 tons (85·65 per cent. SO_3) „ SO_3 = 517·6
Weak acid, 193·3 „ (87·5 H_2SO_4) „ SO_3 = 169·1
Cinders, 179·7 „ (S = 2·3 per cent.) = S = 4·1 tons.

Net SO_3 made in plant = 255·3 tons.
SO_3 lost in plant = 44·2 „
Recovery of sulphur charged = 85·2 per cent.
„ „ burnt = 88·3 „

TENTELEW PLANT (B).

In this plant, which is much smaller and of earlier design than the foregoing, sulphur is burnt in iron pans placed in brick kilns which are somewhat similar to those of the first Grillo plant already described. There are five kilns each

[1] *Second Report on Costs and Efficiencies of H.M. Factories*, 1918, 30.
[2] *Report on the Statistical Work of the Factories Branch*, 1919, 15.

containing an iron pan. The charge for a single kiln may vary between 60 and 120 lb. of sulphur per hour, and the total charge of sulphur in twenty-four hours may vary from 1·3 to 2·6 tons. The temperature of the gas leaving the kilns does not exceed 500°. Leaving the kilns, the gas enters a dust chamber containing two compartments, separated by a partition wall having a hole at the bottom. The inlet is at the top of one chamber and the outlet at the top of the other.

The connections of the various parts of the plant for gas and acid are shown in the diagram of Fig. 115.

The Purification System.

From the dust chamber the burner-gas is led to the burner-gas cooler, which consists of a cylinder of cast-lead 5 ft. in diameter and 10 ft. high, surrounded by a water-jacket extending over all but the first few feet of its height, as shown in the sketch of Fig. 116. At the bottom of the cooler open-spaced bricks are arranged, and above these are fixed four long open-ended, double-walled cylinders, with water circulating between the walls. The gas enters at the top, passes downward through and outside the four cylinders, and after passing through the bricks leaves the cooler by a side pipe. The bottom of the cooler is luted in a leaden tray. The acid condensed in the cooler contains as a rule about 83 per cent. H_2SO_4. The temperature of the gas leaving the cooler is from 70° to 100° and is on no account allowed to exceed 150°.

The two filter-boxes—which follow next in order—are upright cylindrical lead vessels packed with flint on lead grids. Each is fitted with a compressed air-pipe and with a water supply, and with inspection doors. The gas passes through the two boxes in parallel streams, from top to bottom. Acid of from 80 to 90 per cent. H_2SO_4 condenses in them. The sulphur trioxide obtained as condensate from these boxes and from the burner-gas cooler, amounts to 0·9 per cent. of the total made by the plant.

The gas then passes to the washing tower. This is cylindrical, constructed entirely of lead, and is in general similar to that already noticed (Fig. 109). It is 14 ft. high and 3 ft. 9 in. in diameter, and has five sections, *i.e.*, four

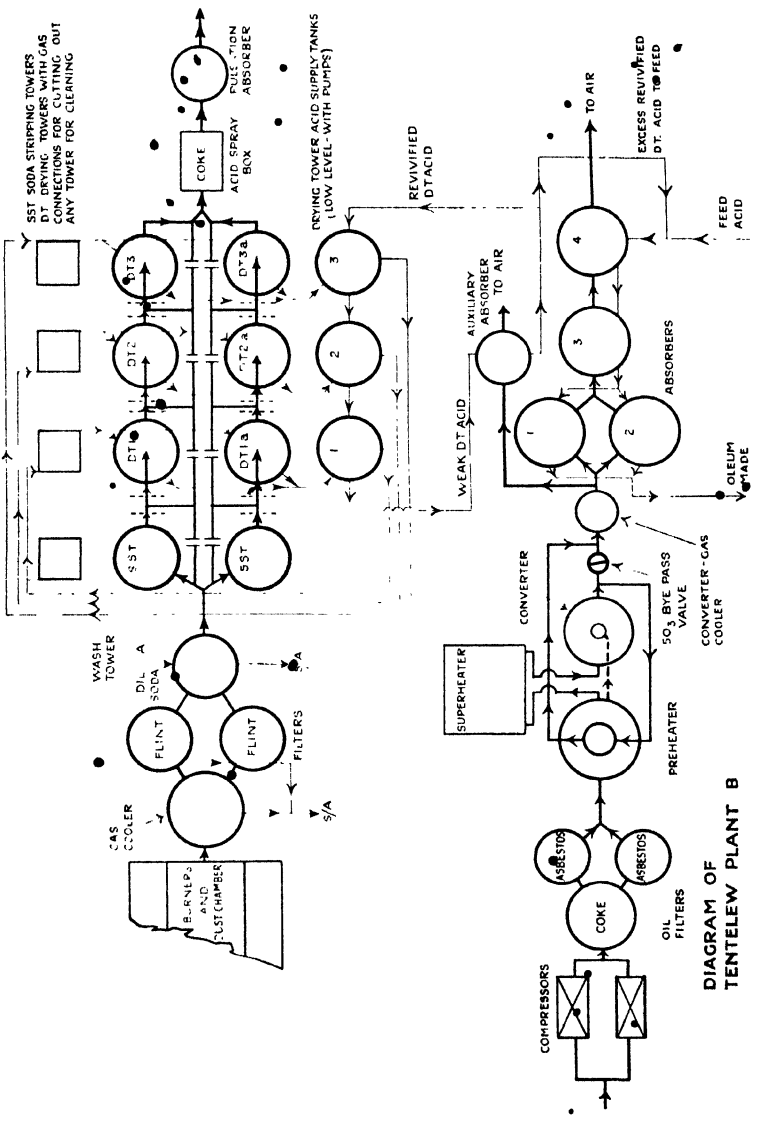


DIAGRAM OF TENTELEW PLANT B

FIG. 115.

bubbling trays. Caustic soda of about ½ per cent. is used, and renewed every twenty-four hours. Each compartment of the tower is connected to that below by a lead pipe which, is kept closed during ordinary running by a rubber diaphragm valve. Manometers are fitted to all compartments so that the amount of soda solution in each one may be estimated

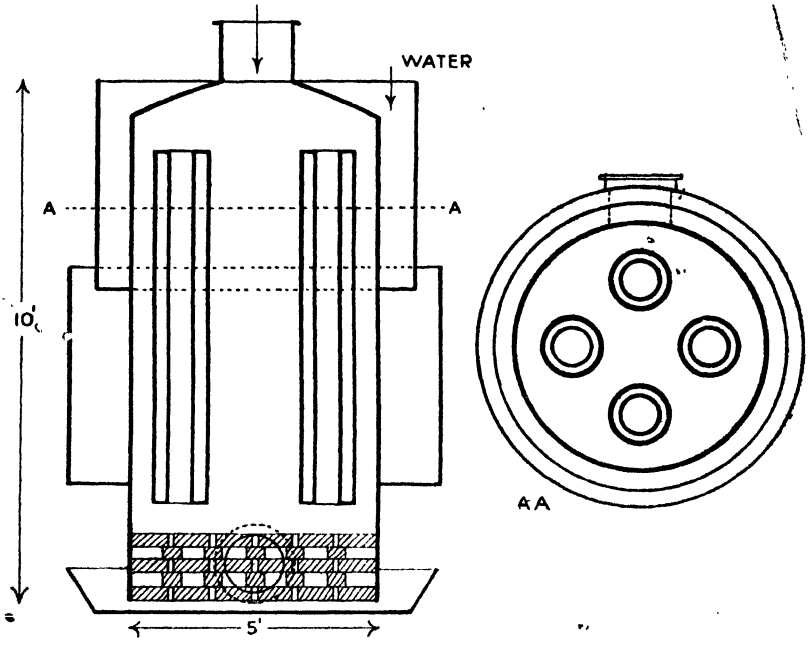


FIG. 116.—Burner-Gas Cooler.

A sampling-pipe and an inspection-door are also fitted to each tray. The liquid which has passed through the tower and run off from the last tray contains sulphuric acid which represents about 5 per cent. of the total production of trioxide.

Two leaden towers are inserted in parallel to remove spray from the washing tower, and each is followed by a set of three drying towers. There are therefore two parallel sets of four towers each. All these are made entirely of lead, and are arranged so that, by means of blind flanges, any tower can be cut out at will for cleaning or repair. As shown in Fig. 117, the bottom of each tower is filled for 2 ft. depth with bricks

in open spacing, and above this is 9 ft. 6 in. of coke packing. The towers are supplied with acid in very much the same way as has already been outlined in connection with plant A, with the exception that a single tower is replaced by the pair of corresponding towers in the two series. From a low-level tank the acid is elevated by a pump to a closed box from which it runs to the appropriate pair of towers. There are therefore three sets of tanks and pumps, and acid is transferred from one set to another by overflow between the low-level tanks. It is supplied to the first tank at about 97 per cent. and leaves the last tank (*i.e.*, the drying tower which the gas enters first) at about 88 per cent. H_2SO_4. Revivification of the diluted acid is carried out in a special small ("auxiliary") absorber. Since the gas leaves the burner-gas cooler at a fairly high temperature, the acid in the first tower becomes hot, and a cooling coil is therefore inserted in the lower tank belonging to this tower.

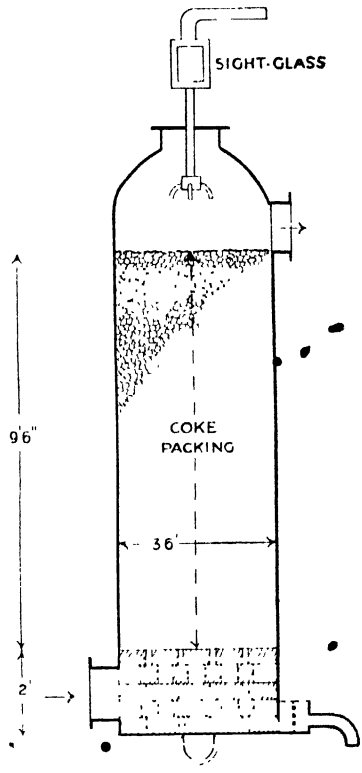


FIG. 117.—Drying-Tower.

Leaving the drying towers, the gas passes through a lead-lined box packed with very fine coke to remove acid spray, and then to an empty lead vessel which serves to lessen the pulsations of the compressor. The whole of the plant and connections, from the entrance to the burner-gas cooler to the inlet to the compressor, is made of lead.

The Conversion System.

This plant has two compressors of the horizontal reciprocating type, having single cylinders lined with gun-metal and water-jacketed. Each compressor is driven by a motor running

at 700 to 900 r.p.m., through a reduction gear which cuts the speed down to $\frac{1}{8}$. The two together, when running at 80 r.p.m., are capable of dealing with the gas from sulphur charges of 2·36 tons. The power required is high. The suction at the inlet is about 3 in. of mercury, and the pressure at the outlet about 10 in.

After the compressors are placed three upright cylindrical tanks made of iron and lined with lead, to act as oil-filters. The gas is propelled first through No. 1, which is packed with large coke, and then passes in parallel streams through Nos. 2 and 3, which are packed with asbestos wool lying on grids. The two streams then unite, pass through a non-return valve, and reach the conversion system proper.

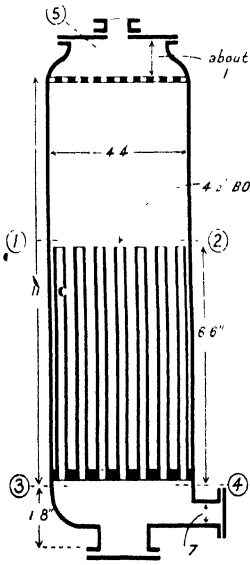


FIG. 118.—Converter.

In this system there are as usual three units—converter, heat-exchanger and superheater, so arranged that the superheater can be cut out during ordinary running. To secure regenerative running, however, is more difficult on a plant of smaller capacity, and in this case superheating is carried out to an extent depending on the particular conditions—size of the charge and so on, as a matter of ordinary practice. On full charge, the superheater requires about 14 cwt. of coal every twenty-four hours.

Both converter and "preheater" are very similar to those illustrated in the Tentelew patent of 1902, as shown in the section on converters. Fig. 118 gives a sketch of the converter. The gas enters at the top and passes through a distributing grid containing 530 holes of about 0·3 in. diameter, into the empty space which occupies about one-third of the volume of the vessel, and then down the 44 contact-tubes, which are 6 ft. 6 in. long and of 4·5-in. bore. The contact-mass is packed in the usual way between perforated discs of malleable cast-iron, each tube having 65 discs.

Pyrometers are inserted at the points numbered on the sketch. The shell of the converter is about 13 ft. long and 4 ft. 4 in. in diameter. The inlet and outlet are of about 7-in. bore.

The "preheater" resembles that of Fig. 25 very closely. It contains upwards of 190 2-in. tubes, 11 ft. 6 in. long, set in two tube plates in a shell 5 ft. 2 in. wide. The cold gas passes over the tubes and the hot gas through them, in the usual way. Both converter and "preheater" are heavily lagged. The superheater is of the same general construction as that of

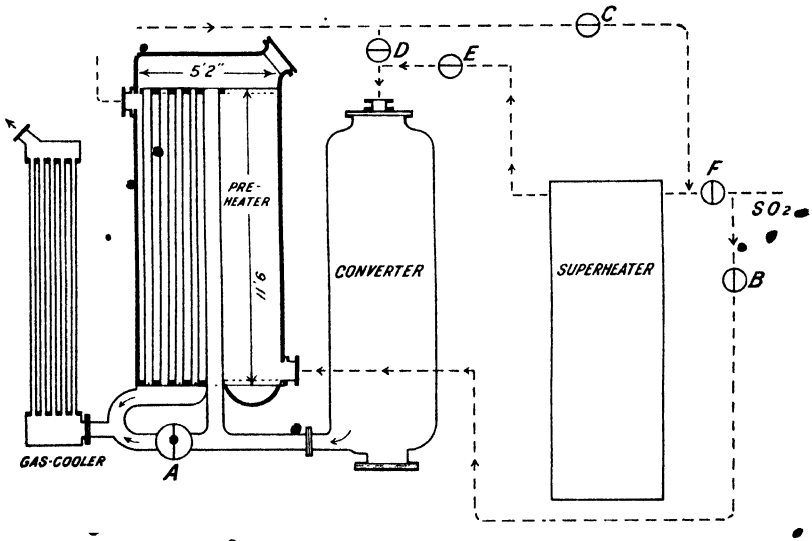


FIG. 119.—Connections of Conversion System.

Plant A, but contains only 42 double tubes, the outer portions of which are 7 ft. 9 in. long. It is fired by coal.

The connections of these three portions of the plant are shown in the diagram of Fig. 119, from which the relative dimensions of converter, "preheater," and gas-cooler may be roughly noted. The valves are shown as set for ordinary running. Purified gas passes, via B, to the outsides of the preheater tubes, then to the superheater, converter, and the insides of the "preheater" tubes in order. The regulator valve A is kept shut. The gas passes through the gas-cooler and goes from it to the absorption system. When the plant is being started, the valves E and F are opened and A B C and D are

closed. Cold gas then passes directly to the "preheater," then to the converter and the insides of the "preheater" tubes, this arrangement being maintained until the converter is hot enough for conversion to begin, when the previous one is established. If the conditions are such that regenerative running is possible valves B and D are opened. C E and F are closed, and A is opened more or less to allow the converted gas, the heat of which is not required, to by-pass the "preheater."

The conversion is usually between 94 and 95 per cent. One converter continued to give 93 to 94 per cent. after seven years' operation, in spite of a slow but continuous decrease. With lower charges higher conversions are naturally obtained. The gas enters the converter at 280° to 300° and leaves at 370° to 390°.

As shown by the pyrometers at the top of the converter (No. 5) and at the outlet, the extent to which the converter acts as a heat-exchanger may be observed in the difference between the average readings (taken over a long period) of No. 5 and Nos. 1 and 2.

Entering Converter No. 5.	Entering Tubes.		Leaving Tubes.		Leaving Converter.
	No. 1.	No. 2.	No. 3.	No. 4.	
290°	384°	390°	389°	396°	382°

Absorption System.

Four absorbers are used for producing oleum, in addition to another smaller one for making acid for the drying towers. Their construction is of the type already outlined (Fig. 113). Each has a single bell which in every case is enamelled. The gas from the cooler passes into the two "oleum" absorbers (1 and 2) which are connected in parallel, then into the remaining two (3 and 4) in succession. The outlet pipe from the last absorber is expanded into a small chamber in which a spray-catching arrangement is fixed. From here the gas escapes to the atmosphere. Feed acid is supplied to No. 4 and runs into the other absorbers by overflow, oleum being drawn off from Nos. 1 and 2.

The drying tower acid is kept in use until it falls to 88 per cent., and is then pumped into a tank feeding the smaller absorber. In this the acid is maintained at about 97 per cent. and the overflow is passed to the drying towers for circulation. The excess of dilute acid received from the drying process, beyond that needed for the drying-tower circulation, is led to a "diluter" in which it is mixed with oleum to form additional feed for the main plant.

The average temperatures of the gas leaving the separate absorbers are:—

Leaving No. 1.	Leaving No. 2.	Leaving No. 3.	Leaving No. 4.
51°	57°	43°	39°

The pressure at various points on the plant are given below in inches of mercury. These figures and the average temperatures given above relate to charges of from $2\frac{1}{4}$ to $2\frac{1}{2}$ tons of sulphur *per diem*.

Pressure Data.

Washing Tower.				Spray-catching Tower.	Entering Drying Tower.			Compressor.		Leaving Absorbers.			
Section 1.	Section 2.	Section 3.	Section 4.		1.	2.	3.	In.	Out.	1.	2.	3.	4.
− 1·0	− 1·7	− 1·9	− 2·3	− 2·3	− 2·5	− 2·6	− 2·7	2·9	+ 10·2	3·5	3·5	2·0	0·1

At the same rate of production (on a charge averaging 2·31 tons of sulphur per day) the overall efficiency of the plant estimated over a period of ten months was 85 per cent. For a previous period of two and a half years, during which the average daily charge had been 1·14 ton, the efficiency had been 87·5 per cent. The acid deposited in the filters and in the washing tower is included as part of the production; if no account be taken of this the figures given must be reduced, by from 4 to 5 per cent.

CHAPTER X

THE MANNHEIM PROCESS

THE origin of this process, in the hands of the *Verein Chemischer Fabriken in Mannheim*, has already been referred to in the introduction, and the characteristics of ferric oxide as a catalyst have been dwelt upon in the discussion of catalytic materials.

The process differs from all other known processes in utilising two catalysts—ferric oxide and platinum, by each of which a part of the conversion is carried out. The sulphur trioxide produced in the ferric oxide contact is absorbed from the gas before it passes, first to filters for the removal of mist and other impurities, and then to the platinum contact. The trioxide produced is again absorbed in a second section of absorbing towers. A peculiar feature of the process, possessed so far as is known by no other, is the drying of the air before it is admitted to the pyrites kilns. This is done mainly to avoid the rapid deterioration of the plant which would result from deposition of sulphuric acid in the pipes and coolers, but partly to prevent the inhibiting action of water vapour on the catalysis at the ferric oxide surface. It is necessary, in order to put this into operation, to enclose the kilns and the brick shafts containing the oxide, in sheet-iron casing, so that ordinary damp air may not be drawn in. Mannheim plants have been worked for years, however, with undried air.

The British and German patents were taken out in the years 1898 to 1901, and the process was adopted some time afterwards by Messrs Nobel at their Ardeer works, who worked six units of plant until shortly before the War, when they adopted the Tentelew process and ceased to operate the Mannheim, restarting it, however, in 1915 for War production. An infringement of their patents by Messrs Nobel was alleged by the *Badische* Company in 1912, in an action brought in

Edinburgh, but was not maintained. The Clayton Aniline Company, Messrs Kynoch, Messrs Levinstein, and the United Alkali Company had all Mannheim plants of pre-war construction, the last named consisting only of the iron contact and kilns worked in conjunction with chambers. In the United States the process has had a considerable vogue.

When the Explosives Factories of the Department of Explosives Supply were projected, batteries of Mannheim plants were included as a more or less temporary measure to fill the urgent need for oleum, which was being imported from the United States in large quantities. This plant was chosen because the designs of the latest type—as used by Messrs Kynoch in their Arklow Factory, and at Umbogintwini in South Africa, near Durban—were ready to hand, and because the type lent itself to rapid construction. These batteries were afterwards superseded by the Grillo, and towards the end of the War were shut down, after having amply paid for their construction. At Queen's Ferry there were ten units (each capable of producing 5 tons of trioxide per day), two of which had Herreshof furnaces to burn smalls; at Gretna there were eight units, also including two Herreshofs; at H.M. Factory, Oldbury, under the management of Messrs Chance & Hunt, there were two ordinary units with lump burners only. Another pair was erected about the same time by the Staveley Coal and Iron Company.

The Mannheim patents have now all expired and possess only slight importance. A concise list of the British and German specifications is given at the end of this section. A certain curious interest attaches to one proposal contained in them, by which the kiln and contact shaft are combined. This is shown in Fig. 120. The bed of burning ore is on the top of the column of contact material, and the dried air passes downwards through the ore. There is no information that this modification was ever in use.

Before proceeding to a discussion of the Mannheim process in its entirety, it may be noted that many installations of ferric oxide contact shafts have been made in conjunction with chambers. Such combinations are in operation at the St Rollox works of the United Alkali Company, where two units, each comprising twelve fires, are in use. The arrangement is in

general similar to that of the complete plant to be described, but there is, of course, no platinum contact, and the gas from the oxide shafts, after passage through three absorption towers, is led directly to the chambers. Containing only about 3 per cent. of sulphur dioxide, it is rather more difficult to deal with than burner-gas of the usual composition, and necessitates a higher nitrous concentration in the chambers. Similar systems are used at the Turnbridge works of the British Dyes Corporation and elsewhere.

In an American plant of this type at Garfield, near Salt Lake City, no attempt is made to produce oleum, the oxide

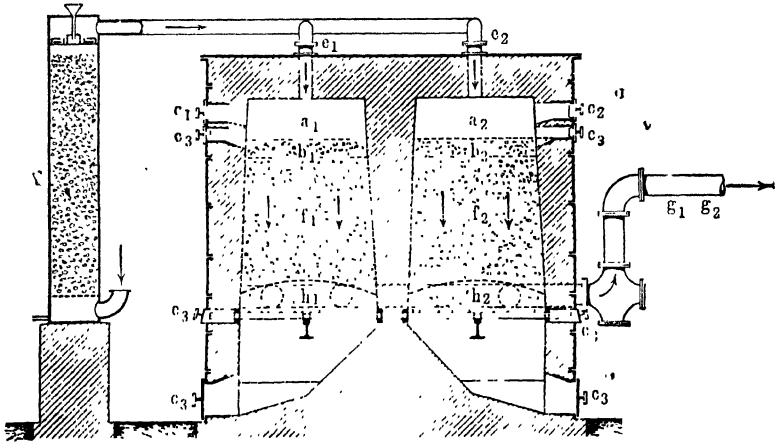


FIG. 120.

shafts being regarded as assistants to the chamber conversion. Herreshof burners are used, each of 20 ft. diameter, and capable of burning 50 tons of ore per day. The burner-gas is led from them through an insulated steel flue, and is delivered to the top of a series of thirty-two burners burning lump pyrites. The gas then enters an oxide shaft 15 ft. in diameter and 30 ft high, and from this passes to the Glover towers of the chamber plants.[1] Another installation has been described[2] of four Herreshof and thirty-six lump burners, the capacity of the Herreshofs being about 11 tons, and that of the others about 16 tons of pyrites per day. The gas from the mechanical burners

[1] *Mineral Industry*, 1916, 25, 692.
[2] Wilke, *Chem. Trade J.*, 1912, 51, 294.

is passed through a baffled flue on top of the lump burners. At the end of this flue both streams of gas are united and pass into the contact shaft, and then to the Glover tower. The conversion in the oxide shafts is about 30 per cent., and the adaptation proved very successful, the normal capacity of the chambers being increased about one-third.

Patents.—Use of iron oxide—as catalyst, B. P. 17255 of 1898, Ger. P. 107995—to remove arsenic, B. P. 17266 of 1898, Ger. P. 106715; kilns, B. P. 1859 of 1899, Ger. P. 108445; dilution of burner-gas, B. P. 3185 of 1899, Ger. P. 108446; combination of contacts, B. P. 24748 of 1899, Ger. P. 136134; other contact substances, B. P. 4610 of 1901, Ger. P. 142410, B. P. 15151; "platinum" contact-oven, B. P. 16206 of 1902, Ger. P. 142855.

1. Construction and Arrangement of the Plant.

The matter of this section has reference, unless it is otherwise stated, to the Kynoch type of plant which already has been mentioned. Very full details have been given, not only in the *Technical Results of Explosives Supply* (No. 5), but also by J. W. Parkes.[1] Both these sources have been drawn from.

The plant is arranged in units, each unit having two separate blocks ("sections") of six kilns, with two iron oxide contact shafts, heat-exchange apparatus, superheater, and platinum contact shaft. There are in addition three gas-coolers, five absorption towers, and a set of filters for each unit. The arrangement is at first sight a complicated one, and the following description may be made more clear by referring to the diagrammatic flow-sheet given in Fig. 121.

Air-drying Towers.—For each pair of units (twenty-four burners) two air-drying towers are provided (Fig. 121). They are built of sheet-lead (from 9 to 12 lbs.) supported on a wooden framework and lined with obsidianite bricks placed without bond, the dimensions being roughly 4 ft. × 6 ft. × 15 ft. high (Fig. 122). The bottom is laid with bricks, and on this is built up a chequer-work which extends to above the gas-inlet, a space being left round the inlet for the gas to enter. On these chequers the coke packing is laid. Into the leaden cover

[1] *J. Soc. Chem. Ind.* (*Trans.*), 1922, 41, 100.

sixteen luted inlet pipes are fixed, and connected in the usual way with a round acid distributor about 16 in. wide and 10 in.

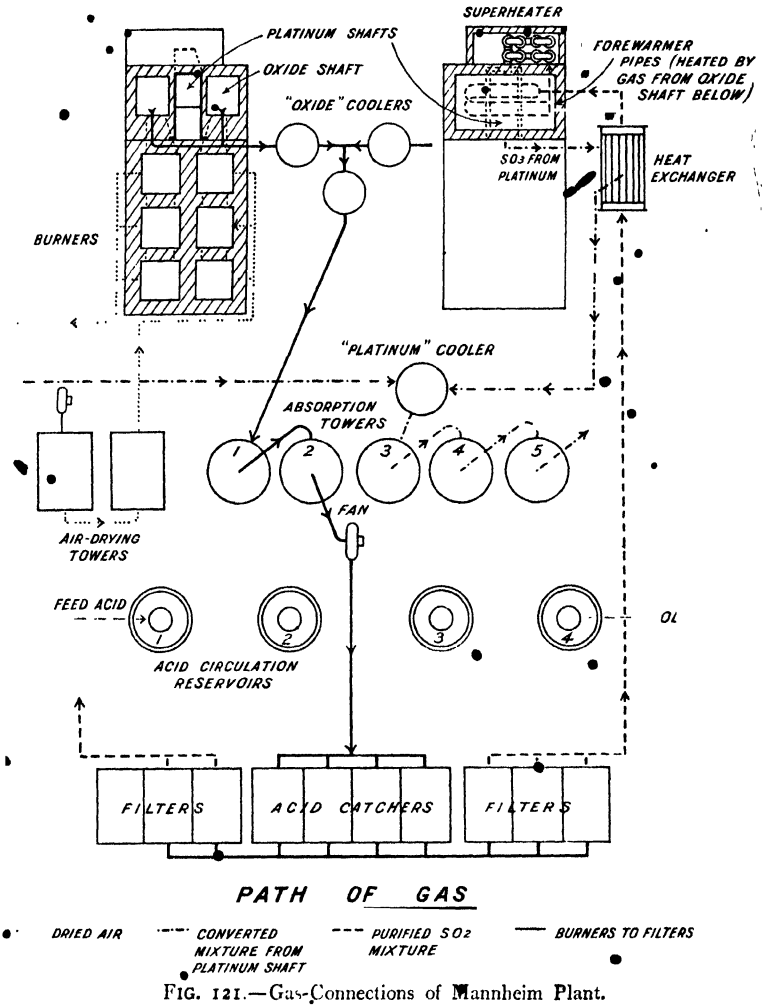


FIG. 121.—Gas-Connections of Mannheim Plant.

high. From a lead-lined wooden tank situated below the floor level, acid of about 94 per cent. was elevated by a cast-iron centrifugal pump to the three feed tanks situated above the three sets of drying towers connected to six units. Down each pair of towers the acid flowed in parallel, and provision was

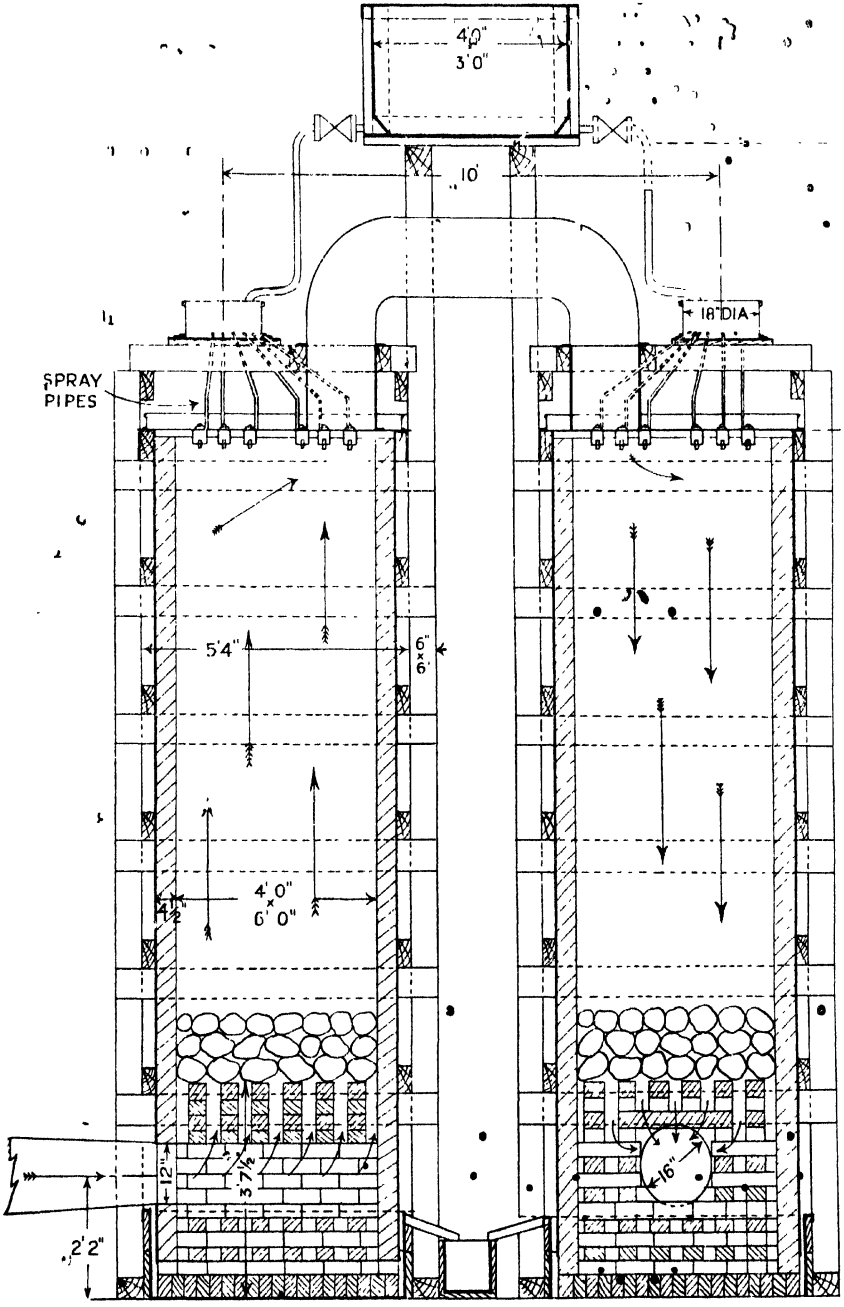


FIG. 122.—Kynoch-Mannheim Plant. Air-Drying Towers.

[*Face pa*

made for running 98 per cent. acid from the absorption system into the tank from which the pump was fed, so that the contents should remain at 94 per cent. This system replaced that of the original design, in which the two towers had each a separate circulating system, the second system receiving strong acid from the No. 1 absorption tank, and the second receiving acid by-passed from the first. The rearrangement resulted in much better drying, but if the object were to secure effective drying with the smallest possible amount of strong acid, an improvement of the original system would perhaps be preferable.

By means of a 12-in. M.V. Sturtevant fan coupled to a 3½ h.p. motor running at 1200 r.p.m., air is blown into the bottom of the first drying tower. From the top of this it passes to the bottom of the second, up, and then to the burners, through a cast-iron main.

The Burners and Contact Shafts.—Each section of lump-burners consists of six kilns placed back to back. Fig. 123 shows a horizontal section through all the kilns. Each kiln is 4 ft. 3½ in. in width and 4 ft. from front to back. The wrought-iron grate bars in which the layer of ore rests, about 7 ft. long and 1⅝ in. square, are rounded to rest on two cast-iron bearer-bars, and can be turned from the outside by means of a key in the usual way. At a height of 18½ in. above the pans is a central charging door; below this, at about the height of the top of the bed, are two raking doors, one on either side, and lower still is a door covering the ends of the grate bars. All these doors are fitted with latches and screw bolts, by which the machined face of the door can be pressed tight against the machined face of the door-frame, the joint being made with asbestos, preferably forced into a milled groove in the door. Under each kiln, at the bottom of the ash-pit, is a cast-iron hopper 3 ft. 4 in. deep, sealed also with a screwed-down door. This hopper projects downward into a basement to facilitate the removal of the burnt ore, as may more readily be seen from Fig. 126, in which, however, the roof of the basement is higher than under the lump-burners. Between each kiln is a dividing wall pierced with an opening 2 ft. 6 in. wide and extending downwards from the arch to about 16 in. above the firebars. The whole section—kilns, contact shafts, etc., is encased in a thin shell of steel plates riveted to a steel framework. The

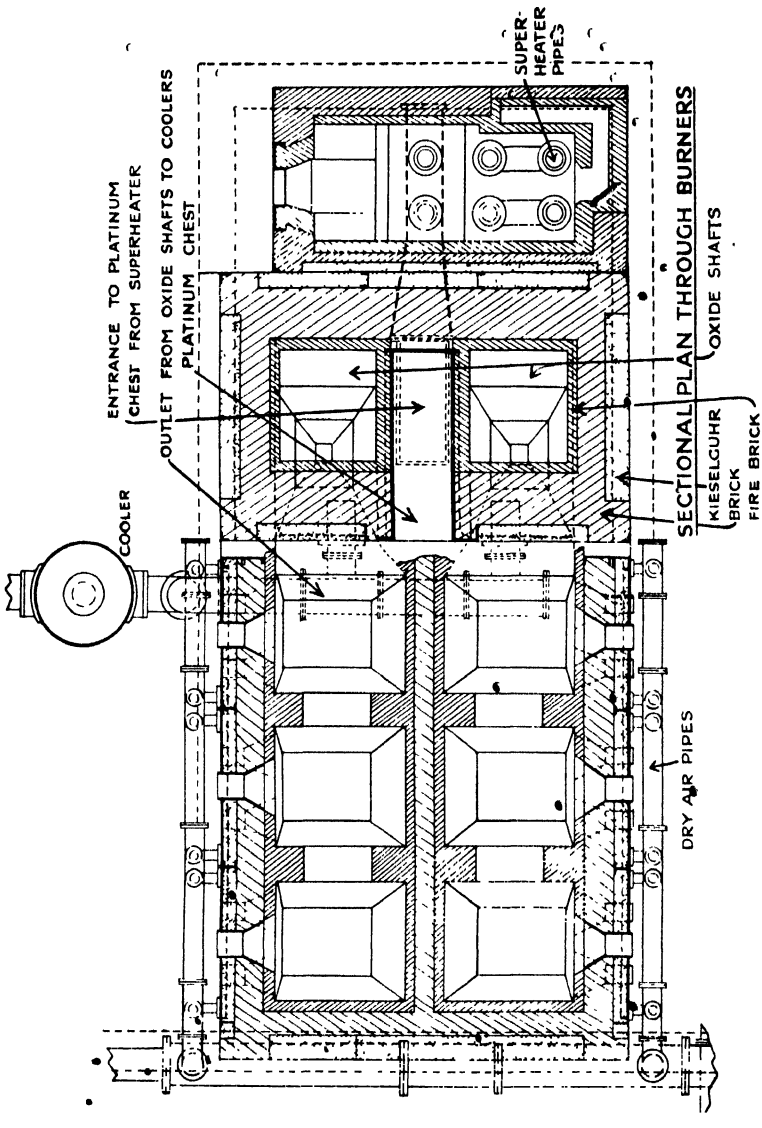


FIG. 123.—Pyrites-Burners of Mannheim Plant. Kynoch Pattern.

casing is made air-tight by caulking with asbestos cord. The dried air enters each kiln through two 4-in. cast-iron pipes below the bars. Each pipe carries a butterfly valve and has a flange on the lower T-piece for clearing out dust.

The design of burner may be compared with that shown in the sketch of Fig. 124. This pattern is that of Mannheim plants built soon after the date of the patents, some of which

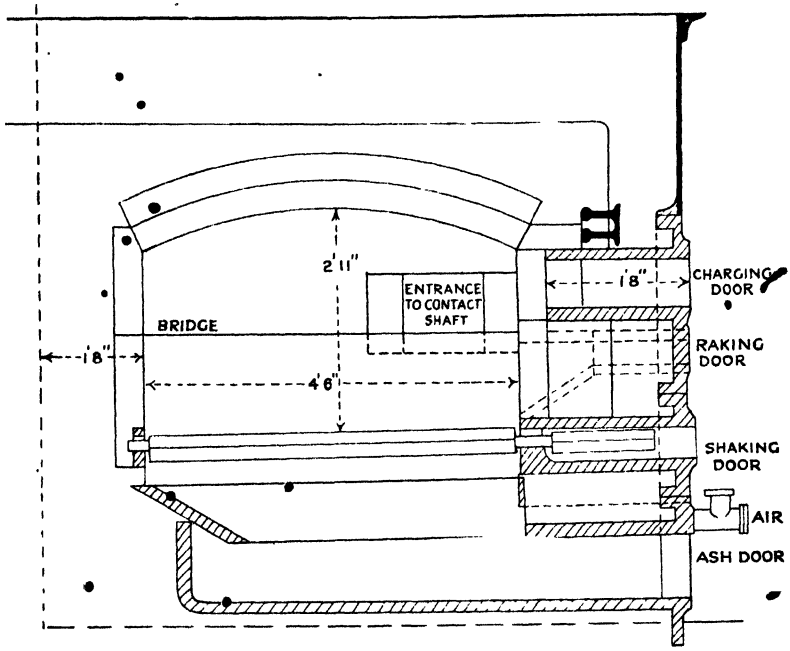


FIG. 124.—Mannheim Pyrites-Burner (Old Pattern).

are still in use. There was no lower hopper, and the burnt ore fell into iron boxes in the ash-pit, or was simply raked out. Instead of six burners in a section there were eight.

The Herreshof burners fitted to the units on which smalls are to be burnt are of the standard type, with fire hearths of about 10 ft. internal diameter—the total hearth area being about 385 sq. ft. The heavy cast-iron hollow shaft—about 20 in. diameter—is perforated with ten slotted openings, into which the hollow rabbling arms are fitted, each hearth having two arms. The ore passes inwards, through the slots to the

next shelf, then outwards and so on, in the usual way. The shaft weighs 3 tons and is borne on a ball-bearing at its base. It is rotated at the rate of a revolution in a little over two minutes by a 2 h.p. motor connected by bevel gear and sprocket-wheels. The automatic feed is of the plunger type. The cinders fall from the lowest hearth into a cast-iron hopper. These burners are shown in Fig. 125 and Fig. 126.

The dried air is introduced to the lowest shelf by means of four small openings near the base of the shaft. The air-main is connected with the top of the hollow shaft by means of a luted collar. The air passing downwards, cools the shaft and arms and reduces the danger of overheating.

The temperature of the gas leaving a Herreshof burner, when the sulphur dioxide is about 5·5 per cent., is too low (670° to 680°) for satisfactory conversion in the oxide shafts. The gas therefore leaves the upper shelf by two openings (2 ft. 7½ in. wide and 9 in. high), from each of which it passes into two lump-burners built back to back and identical with those already described.

Each section of lump-burners, or each section containing a Herreshof burner, has two iron oxide shafts of about 4 ft. square section and 11 ft. 6 in. high, with grate bars at the bottom, and a hopper just as in the case of the burners. The grate bars, however, being larger, are borne on three bearers instead of two. The gas from the single row of burners passes into the oxide shaft through an opening in the dividing brickwork, passes upwards through the lumps of oxide, then through chequer holes in the arched roof into the chamber containing the "forewarmer" pipes. This chamber is about 10 ft. long, 6 ft. wide, and 5 ft. high, and has a central baffle wall about 3 ft. 6 in. high dividing it in the direction of its length. The chequer holes are all behind this wall, *i.e.*, to the left-hand side of it in Fig. 126, so that the hot gas from the two shafts passes up over one set of pipes, over the top of the baffle wall, and down over the other set. The outlets to the chamber are two short 14-in. cast-iron pipes connected by a 14-in. main. T-pieces are fitted to facilitate cleaning out the dust. The "forewarmer" pipes will be encountered later. See also Fig. 127.

The Coolers.—The gas from each pair of oxide shafts is conveyed by the cast-iron main to a cooler (already illustrated

in Fig. 80), which consists of a simple steel cylinder 3 ft. 8 in. in diameter and 16 ft. 8 in. high. It is fitted with three

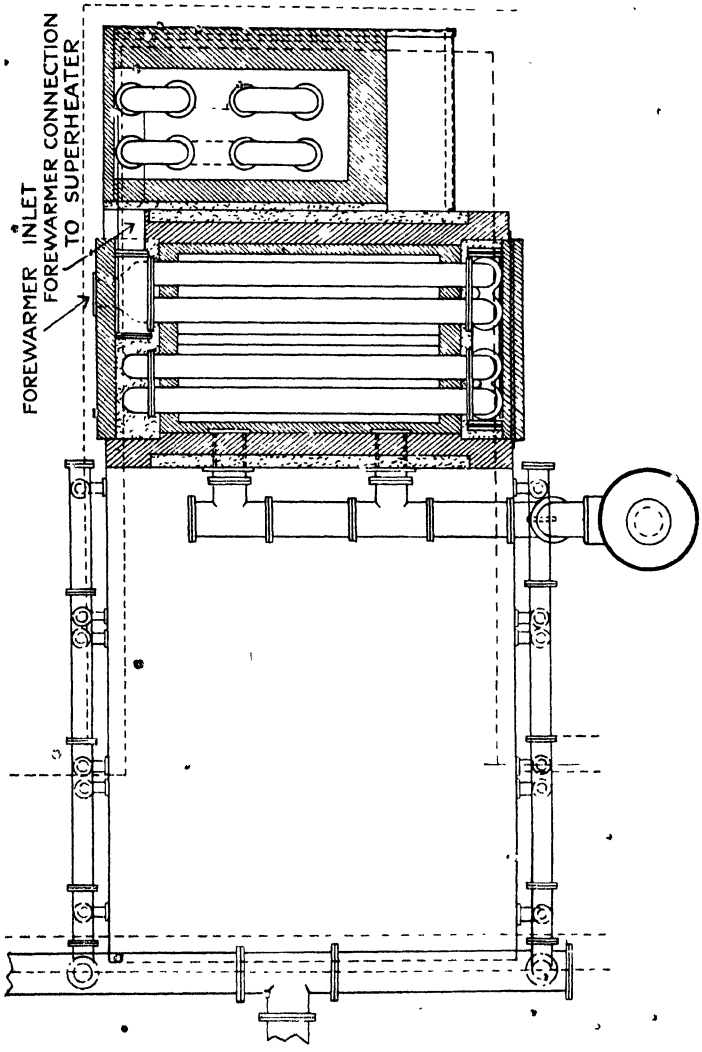


FIG. 127.—Horizontal Section through "Forewarmer" and Superheater (Lump Burners).

horizontal internal baffle plates about 3 ft. in diameter and nearly the same distance apart, by the action of which the hot gas is mixed and thrown outwards against the sides. The cooler has a cleaning door and a dished top with serrated edges

to distribute the water, and stands in a large leaden saucer. To two of these coolers is joined a third through which all the gas from the two sections passes to the two towers constituting the first absorption system. In this the trioxide formed by the passage over the heated ferric oxide is removed. The absorption system as a whole will be reserved for discussion a little later.

The acid from the coolers is drained to a settling tank. It was found to be an advantage to alter the original arrangement of drain pipes, and to substitute wide cast-iron pipes luted into the tank, and so fitted that each section of pipe could be cleaned out readily. This can be seen in Fig. 125.

The Main Fan.—The gas is drawn through the plant so far described, and forced through the rest under slight pressure, by a Kynoch fan. The function of the fan mentioned before is only to impel the air through the drying towers, and to neutralise, with a slight pressure, the suction which would otherwise exist at the burners and allow damp air to be drawn in. The Kynoch fan consists of a cast-iron casing in two halves bolted together, inside which rotates an impeller 2 ft. 1½ in. in diameter, fitted with sixteen concave cast-iron blades 7¼ in. wide and of peculiar shape. The shaft is connected through a flexible coupling with a 6 h.p. motor, which is preferably of variable speed, with a maximum of 1650 r.p.m. The air enters the fan at the centre through a 12-in. cast-iron main and leaves tangentially at the bottom. A drain is provided for the condensed acid. The fan is capable of dealing with about 1,600,000 cub. ft. of air per day at a pressure of 4 in. and a suction of 2 in. of water.

The Acid Catchers and Filters.—Leaving the fan the gas from the twenty-four fires is forced through four acid catchers in parallel. The two streams issuing from each pair of these vessels, pursue from this point separated but similar paths, each passing through three filters in parallel, and then being delivered to the preheating apparatus of one section. Each catcher or filter is a steel tank 11 ft. 6 in. long, 6 ft. 6 in. wide, 4 ft. 1 in. deep, and fitted with a grid 8 in. from the bottom, formed with steel bars laid on bearers. The gas-inlet and outlet are of 8-in. bore. At the bottom a luted drain-pipe is fitted which drains into a tile-lined launder common to all the tanks. The acid running from this, and from all the coolers

and the fan is highly arsenical, and was always removed from the plant, and in many cases utilised for nitric acid manufacture.

The packing of the acid catchers is of graded quartz. The grid may be covered with a layer of 3 to 4-in. lumps, on which is placed a 4-in. layer of material graded from $2\frac{1}{2}$ in. down to $\frac{3}{8}$ in. The main bulk of the filling is a layer 18 in. in height placed on top of the $\frac{3}{8}$-in. size, and consisting of fine stuff graded from $\frac{1}{4}$ in. to $\frac{1}{16}$ in. Finally, a 3-in. layer, $\frac{1}{10}$ in. to $\frac{1}{30}$ in. in size, is spread over the main filling. The filters are packed with quartz in the same way until the $\frac{3}{8}$-in. material has been put in, but on this is laid granulated basic slag rich in lime. Each filter has 18 in. of slag graded from $\frac{1}{8}$ to $\frac{1}{16}$ in., and finally 5 in. of dust-free material passing $\frac{1}{16}$ in. mesh. A typical analysis of the slag sand is: CaO 47·3, MgO 0·9, Al_2O_3 14·9, Fe_2O_3 5·6, SiO_2 29·2 per cent.[1] In many plants a layer of asbestos fibre and lime is placed on top of the slag sand.

After some time the acid catchers become clogged and must be emptied and cleaned. The quartz is washed and replaced. The life of the filter-packing is variable, but it requires renewal at intervals, the length of which depends on the result of the tests made to ascertain the efficiency of purification. Any one acid catcher or filter can be isolated from the others by the insertion of blind flanges in the connecting pipes.

The Preheating System.—The course of the purified gas during preheating and conversion can be seen in outline in the flow sheet of Fig. 121. In this figure, for the sake of clearness the platinum contact is shown in only one section, and the ferric oxide shafts appears alone in the other. The flow of gas may also be studied in the plan (Fig. 125) and in the elevation (Fig. 126) of the Herreshof unit. The cold purified gas passes in succession through heat exchanger, "forewarmer," and superheater. The heat exchanger is in every essential respect the same as that already described in connection with Grillo plants, see Fig. 38, p. 177. Cold gas from the filters passes by two separate pipes to the inside of the heat-exchanging tubes, which are maintained at a temperature of about 200°, by the passage of the hot converted gas over them, and then enters the "forewarmers" situated in the brick

[1] Parkes, *loc. cit.*

chamber which is above and in communication with the oxide shaft. The inlet to each "forewarmer" is a 12-in. pipe which inside the casing divides into two 10-in. cast-iron lines which are carried six times across the chamber parallel to the baffle wall, the ends of each pair being connected to the next pair in the series either by a header or by two U-bends. The exit is by a header at the bottom of the chamber at the same side, and under the inlet. This header is continued backwards to the superheater. See Figs. 126 and 127.

The superheater, as may be seen from the figures last noted, consists of six vertical 10-in. cast-iron pipes about 11 ft. 6 in. long, forming two parallel series of three pipes each. The upper joints of the connecting double bends are outside the arch of the chamber, and the lower joints are protected from the fire by a bridge. The two last pipes of each series (in which the gas descends) are connected to a lower header which extends to meet the inlet to the back of the "platinum" chest. This header is encased in brickwork. The pipes have a heating surface of approximately 40 sq. ft. ("forewarmer," 80 sq. ft.). The superheater chamber is divided by two dividing walls into three flues, so that the flue gas passes along each row of two pipes in succession, and in the usual countercurrent to the gas inside them. A steel pipe from the head of the last flue acts as a chimney and projects through the roof of the house. On the large installations these small chimneys were all replaced by one large one outside, connected with the flues by a 20-in. sheet-iron main.

The superheater pipes as described are apt to give rise to leaks from springing of the joints under the action of the heat, and many rearrangements of them have been tried on other Mannheim plants. One of the most successful of these is perhaps the substitution of "pistol pipes." These are pipes of oblong section with an internal longitudinal feather, the gas passing up the feather on the one side and down on the other.

The Platinum Chest is placed between the two oxide drafts and is made up of five cast-iron sections with machined joints, bolted together with asbestos jointing. The lower section, 49 in. from back to front, contains an oval inlet 22½ in. wide and 9 in. high. The three middle sections in which the

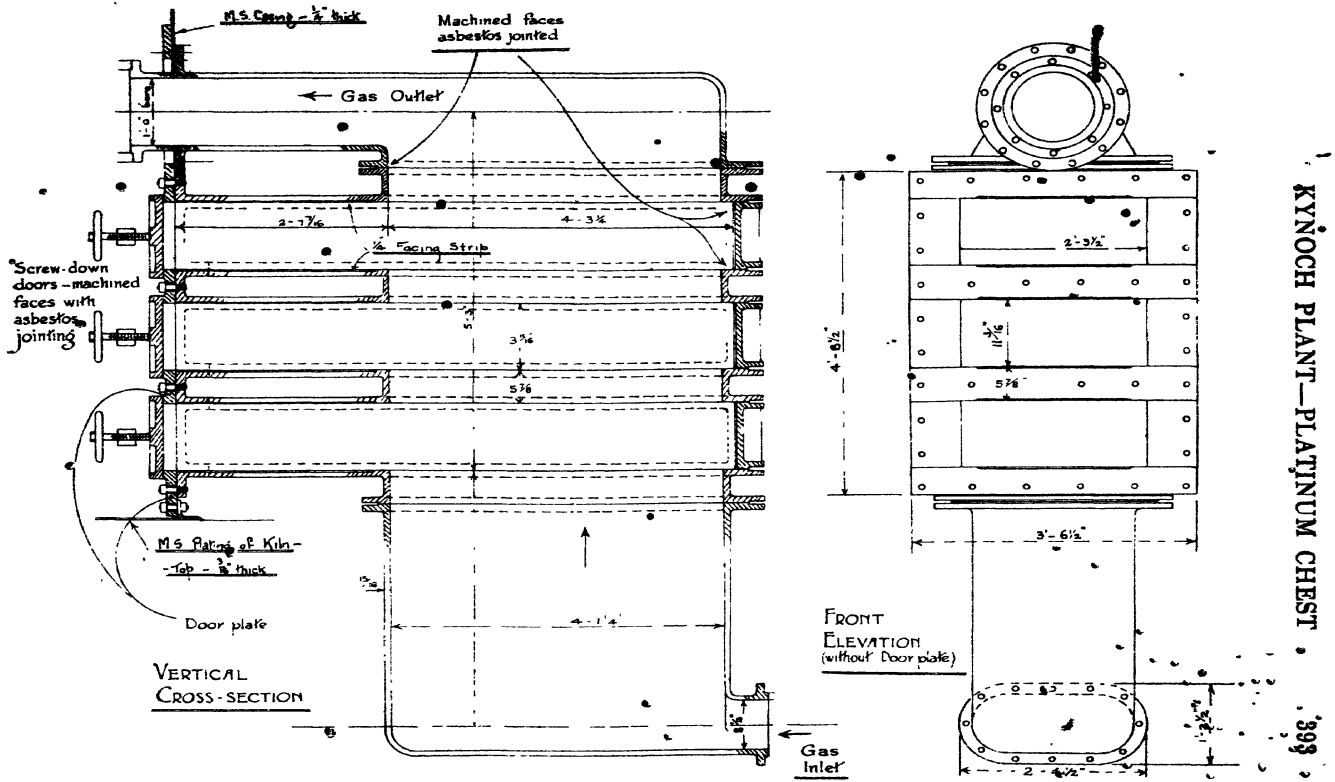


FIG. 128.—Mannheim Contact-Chest.

elements of mass are placed are mounted one on another, each being 11¾ in. deep, and are crowned by the prism-shaped top section bearing a 12-in. gas outlet. All the sections are bolted to a heavy door-plate with screw-down doors to close each chamber. The cross-section may be examined in Fig. 128, which represents a chest the dimensions of which differ slightly from that of the Kynoch plant, but which is similar in design. The left-hand sketch gives a vertical cross-section; the right hand a front elevation, the doors and door plate having been removed.

In each section the ledges in which the element rest, as well as the frames of the element, are machined, and as the element is pushed in hard against the back of the chest, a fairly gas-tight joint results. The gas enters at the bottom, behind, passes upwards through the elements, and leaves at the top, in front.

An element is built up between two cast-iron frames, the dimensions of which are shown in Fig. 129. Each of the ten asbestos mats is laid on a grid of iron wire gauze of ¾-in. mesh and 14 I. W. G., and separated from the next by a steel frame plate about $\frac{5}{16}$ in. thick. The ascending order is therefore: frame, gauze grid, mat, frame plate, gauze grid, and so on. The whole is held together by eight bolts.

The preparation and preliminary treatment of the platinised asbestos mats has already been described in Chapter IV. The weight of platinum employed on each mat, on most plants during the War, was 20 or 24 gm. That is, on the 60 mats required for an element there were between 1·2 and 1·44 kilos. The amount of platinum used is low in relation to the work required of it, as may be seen from the table at the beginning of Part 2, Chapter IV.; and in some plants thirteen nets have been used in an element instead of ten. This change necessitates thinner distance-frames. On some units also, auxiliary contact-chests designed to hold a single element have been built in a readily accessible position.

The position of the platinum chest between the two oxide shafts is a bad one, and a redesigned plant would certainly have the chest somewhere else. Leaks invariably begin at one or other of the many joints, and repairs cannot be carried out without pulling down the brickwork which nearly surrounds

the chest. No platinum chest which has been in use for some months is tight, and the arsenical gas from the oxide shafts finds its way in and hastens the poisoning of the elements.

From the two platinum chests the converted gas passes by separate pipes to the single cooler, which is identical in size and shape with those used for the gas from the oxide shafts. On the way to this cooler the gas is deprived of some of its heat by passing over the pipes of the two heat exchangers, and falls in temperature from 480°-500° to 320°-300°. It then enters the three towers which form the second section of the absorption system. The first section consists, it will be remembered, of those two towers which received the gas from the oxide shafts.

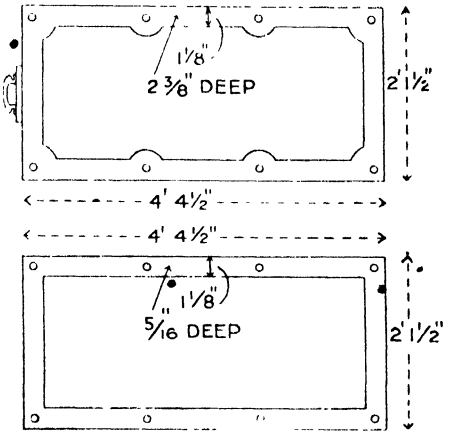


FIG. 129.

The Absorption System.—The five towers are similar in design, construction, and packing to the towers of the D.E.S. Grillo plant already described, but in this case the whole five are erected on the concrete platform in one row. At the foot of the towers are four steel acid reservoirs 6 ft. in diameter, 2 ft. 11 in. high, erected at a height sufficient for feeding to the four centrifugal pumps which are in pairs between the reservoirs, each pair being driven by a single motor. This layout can be inspected in Fig. 125. Each reservoir is fitted with a cast-iron lute box in the centre of the cover, into which the acid returning from the towers is run, and all except the first in the series are fitted with steel water-jackets.

The towers are numbered 1 to 5 in the order of the gas stream; the customary numbering of the acid tanks is in the same direction. The essential points of the system may be seen in the diagram (Fig. 130). Feed acid is run into No. 1 tank, and from there elevated into the feed boxes at the head of towers 2 and 5, returning mainly to the same tank but partly flowing into the next (No. 2) by means of the

pipe connecting the two feed-boxes on the tanks. All these connecting pipes are controlled by valves, so that acid can not only be passed forward, but backwards as well. From No. 2 tank, tower No. 1 is fed; from No. 3 tank, tower No. 4; and to No. 4 tank, tower No. 3 is connected, in which the greatest amount of absorption occurs. The return from tower No. 3 is connected not only to tank No. 4 but to the feed-boxes of tanks Nos. 3 and 2, and sometimes to tank No. 1 also. The acid in any of these can be strengthened with oleum if necessary. The delivery pipe from the pump

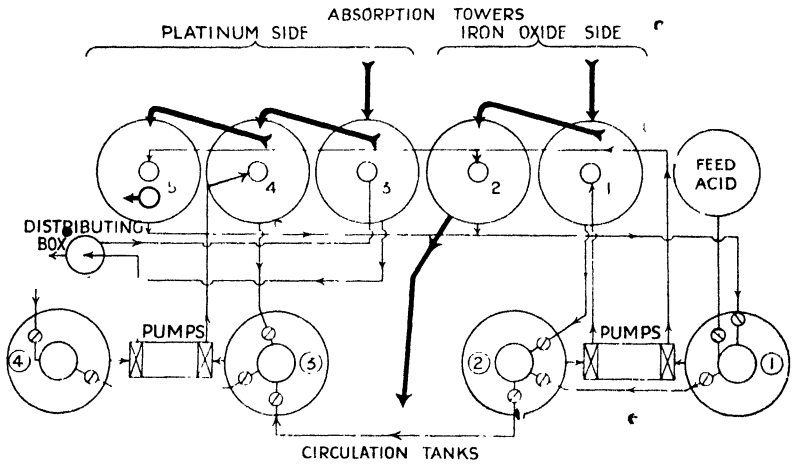


FIG. 130.—Kynoch Plant. Acid Circulation System.

connected to tank No. 4 has a branch leading to a high level sight-box, through which the stream of oleum running to storage from the unit can be seen.

The circulation system of the Kynoch plant, which has been shown in the diagram only in a simplified form, is largely dependent on the adjustment of numerous valves on the return and forwarding pipes. It is very flexible, and with practice the adjustments are readily made and infrequently altered; but on the whole the system requires, comparatively, a good deal of attention, and there seems no adequate reason why automatic overflows from tank to tank should not be fitted. This, indeed, was done many years ago on at least one large plant, and worked successfully. For strengthening

the acid in the weaker reservoirs when necessary, suitable by-passes could easily be provided without the present complication of piping. It would probably not be easy to reduce the number of reservoirs, on account of the concentration of nitrioxide vapour (and consequently the strength of the acid which can increase in strength on circulation) being different in nearly all of the five towers.

Some Mannheim systems of older design had six towers,

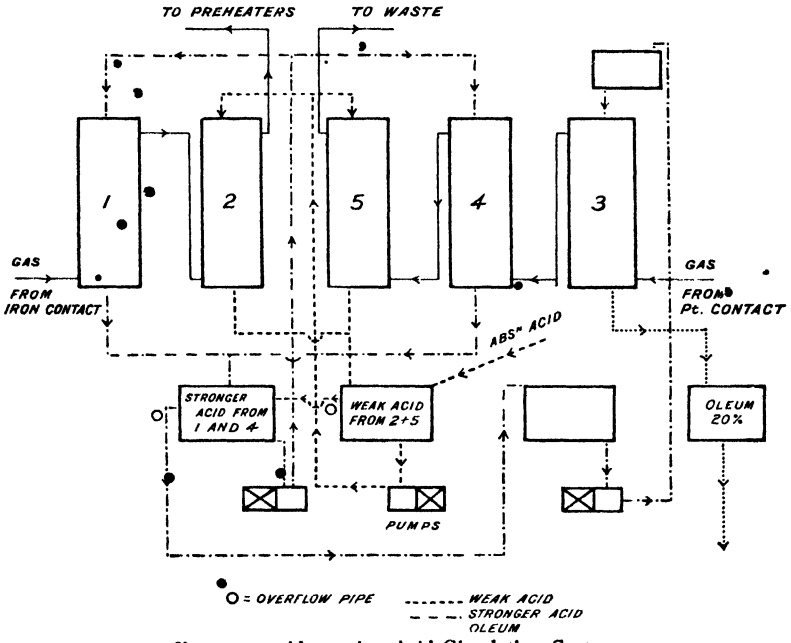


FIG. 131.—Alternative Acid-Circulation System.

three for each contact, the two first towers being combined with a single tank, the two second with another, and so on. There were then three circulation tanks, and by the provision of overflows the circulation had comparative simplicity. So many towers, however, are unnecessary. Employing five towers, the same arrangement can still be maintained, with the exception that the acid in the odd tower (No. 3) is not, properly speaking, circulated at all, but is run straight through once and for all. This system which worked well in practice, is shown diagrammatically in Fig. 131. Towers 1 and 4 were connected

to tank No. 2, towers 2 and 5 to tank No. 1. Feed acid of about 94 per cent. was run into No. 1, and was raised in strength in towers 2 and 5; overflowing to tank No. 2 it again became more concentrated in towers 1 and 4. From tank No. 2 it was raised to a feed tank above tower 3, and allowed to run down at such a rate that it passed out at the bottom as 20 per cent. oleum. No attention was necessary except to the feeds to the tower and to the first tank. There is no reason why towers 1 and 4, and the feed tank above tower 3, should not all be fed from the same pump. Three tanks and pumps (including the pump for removing the oleum made) would then suffice.

For all the pipes, cast-iron is preferable to steel, except for the delivery to and return from No. 4 (oleum) tank. A suitable size for the delivery is $1\frac{1}{4}$ in., and for the returns $1\frac{3}{4}$ in. Smaller return pipes than this are apt to run too slowly and cause the towers to "choke," *i.e.*, fill with acid to above the gas-entrance pipe, when the feeds are heavy. With towers of the usual size, and the small output of the Mannheim unit, the advantage of counter-current flow becomes less than on other types of plant. Experience has shown that a battery of towers connected by short pipes alternately at top and bottom is scarcely less efficient than when the usual connections from top to bottom are fitted.

2. Operation and Control.

The Burners and Oxide Shafts.—The usual thickness of the bed in the Mannheim plant lump burner is about 10 in. Thicker beds, up to 20 in. can be used, but experiments carried out at Queen's Ferry showed that the fires of the usual depth were easier to work, especially by inexperienced burner-men, more free from clinker, and more easy to restore when the dropping of the burnt ore from the bars had not been carried out properly.[1] The ore used is in lumps which all pass a 2-in. ring, and have passed over a screen with $\frac{3}{8}$ to $\frac{3}{4}$-in. holes, according to the amount of fines which must be included with the lumps. Hand-broken ore is of course preferred on account of its more even size and shape,

[1] *T.R.E.S.*, 1921, 5, 11.

but more usually, as in the installations referred to, the ore comes from a crusher, the fines being fed to the Herreshof furnaces. In breaking Peña ore at Gretna it was found that the proportion of $\frac{3}{8}$—2-in. lump, to fines not exceeding $\frac{3}{8}$ in., was as 68 to 32. With hand-breaking only 10 per cent. of the smaller size was produced. This ore was employed on account of its low arsenic content.

The operation of the burners consists of three processes—charging, raking, and dropping (*i.e.*, turning the grate-bars to allow the burnt ore to fall through them)—which are carried out on each fire in regular rotation. As to charging, it is essential to make sure that the same amount of ore is always charged to every fire; counting by shovelfuls is unreliable, and each charge, or at least each pair of charges, should be weighed or measured in a specially made box. If this is not done, some fires burn out before their time; others are still burning when they are charged, and clinker may form as a consequence. A single charge may vary from 2 cwt. to 2·5 cwt., and in some cases may be more. It is dropped in from the charging shovel (Fig. 132), beginning at the front and working evenly towards the back. This and the subsequent operations should be performed as rapidly as possible to avoid the access of damp air to the kiln, although if the damper of the fan driving air into the kiln is properly adjusted, very little air should pass either in or out. Three hours after a fire has been charged, it is raked with a single pronged rake (Fig. 132), and this operation is repeated after two hours more, *i.e.*, an hour before the time of the next charge. In raking it is important to bury the whole prong of the rake in the ore, so that the dust may be shaken down to the bottom of the bed. It is also very advisable to rake each fire in some definite way. Beginning, for instance, at the left-hand raking-door of any fire, the rake is inserted at the furthest accessible point of the burner-wall on the right-hand side, and is then drawn to the middle line of the fire. Then it is inserted with the point of insertion a little further to the left. The front of the fire is then raked as far as the middle line, the rake this time being pushed. The whole procedure is then repeated from the other door. This method removes from the back and sides of the furnace the dust which is apt to collect there. Finally, the fire is levelled with the double-pronged rake.

The dropping of these thin fires must be most carefully done, and requires trained men. The key (Fig. 132) is slipped on to each bar and is quickly turned five or six times

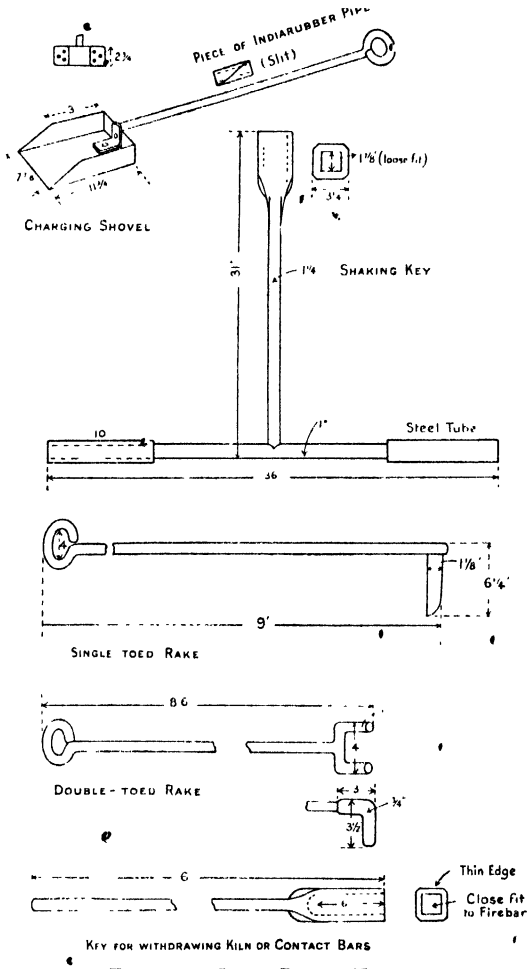


FIG. 132.—Lump-Burner Tools.

40°. If a bar is stiff it is not turned through a greater angle, but the next bar is turned slightly and left on the flat while the first is moved. Each bar is finally left on the diagonal, edge upwards. The usual time of dropping fires was one hour before charging. Each fire was therefore dropped once

in six hours. On some Mannheim plants this was not found necessary, and one dropping in twelve or even twenty-four hours sufficed.

Manipulating the burners in the way which has been described, clinker never forms, and when the kilns are doing steady work Peña ore can be burnt down to 3 per cent. of sulphur in the residue, and even in some cases to 2 per cent. This result is of course not possible with all ores.

One burner-man can attend to the twelve fires of one unit. A suitable charging order for the burner is shown in the diagram below, the numbers indicating the time of charging throughout the twelve hours. Raking is carried out three hours, and also five hours later. It will be noticed that the fires of the second section are timed at half-hours. This is to cause the fluctuations in gas composition, which occur when every fire is charged, to neutralise each other as far as possible; charging every half-hour means that only one fire, instead of two, is charged at a time. The burner-gas concentration curve for the whole unit is made flatter, for of the peaks which occur (one from each newly charged fire) no two coincide.

1.	6. 1 7	7. 2.30 8.30	12. 1.30 7.30		
2.	5. 6 12	8. 3.30 9.30	11. 6.30 12.30		
3. 4 10	4. 5 11	9. 4.30 10.30	10. 5.30 11.30		

The Herreshof furnaces call for little special remark. Each is capable of burning about 3 tons of ore in a day, and the four lump burners of a Herreshof unit are charged and run in the usual way. The total capacity of the unit is therefore about 8 tons per day. Ore containing too much dust should not be used on account of the choking of the oxide shafts, which is more apt to occur than with a lump-burning kiln. The lump burners of a Herreshof unit are more trouble to keep in order than the others, partly on account of dust, which tends to make them dull. The third shelf of the rotary burners is the hottest,

the second should be distinctly red, and the last should appear quite dead and black.

The oxide shafts are charged with burnt ore which has been passed over a screen to remove pieces of less than 1 in., and it is preferable to use cinder which has been recently dropped and is still hot. Each shaft holds about 7½ tons. It is usual to drop about 2 in. from each shaft once in twenty-four hours, but this amount may be varied in view of two considerations—that the arsenic content of the cinder taken out is not allowed to rise above 2 or 2½ per cent., and that the shaft may tend to become blocked with dust, as indicated by the difference in pressure at the inlet and outlet of the shaft.

The average of the conversion in the shafts varies from 30 to 40 per cent., and is said sometimes to rise to 45 per cent., but not to exceed this in ordinary circumstances. The conditions of temperature and gas concentration which are most favourable are not well known, and tests of the conversion are not easy to carry out in a reliable way. (See the discussion of ferric oxide as a catalyst in Chapter IV.) It has been found in many cases that for a burner-gas of the usual average composition (5·5 per cent. SO_2), with good ordinary conversion, the highest temperature reached in the shafts lies between 700° and 750°, about half way up. The ore must be evenly sized and freshly burnt. There is agreement between the results of the researches on ferric oxide catalysis and the conclusions of those conducting the process, in that the presence of water has been found in both cases to diminish the activity of the mass, as well as to cause, in practice, much trouble from the formation of sulphate.

As in the case of the Grillo converters already described, the intermittent charging of the lump burners gives rise to wide fluctuations in the gas concentration. These are, to a large extent, "smoothed out" by the unison of the four separate streams in the "oxide" coolers, and this process can be assisted by adjustment of the charging times, as already indicated. In the shafts themselves, however, these fluctuations are extreme and the conversion is unfavourably affected, for each rise in gas concentration causes a fall in conversion, and *vice versa*, so that the ferric oxide never settles down to steady work. These changes are very similar to those which occur in Grillo

converters in connection with hand-charged sulphur-burners, and like them, are to be avoided only by adopting mechanical and continuous burning.

The Purification System.—The process of purification in the Mannheim plant not only depends on the acid catchers and filter-boxes exercising their usual function of retaining acid mist, but is also involved with the action of the oxide shafts. In these the greater part of the arsenic is trapped, but the gas is also charged with sulphur trioxide, which the first half of the absorption system has then to remove. The concatenation of the preliminary air-drying results in the gas being of extreme dryness at the entrance to the filters, but laden with acid mist containing a high percentage of sulphuric acid. It is always necessary to bear in mind that success depends always on the use of acid approaching 98 per cent. in the second tower, for if the absorption here is incomplete, the acid catchers and filters receive, if not free trioxide which they are in no way designed to absorb, at least an abnormal amount of arsenical acid mist.

By means of efficient air-drying the amount of water entering the burners can be kept down to 0·30 gm. per cubic metre; if this figure is adhered to, the acid deposited in the "oxide" coolers attains a strength of about 10 per cent. of free trioxide and is small in quantity; the formation of sludge is also very much diminished. The following figures show the relative amounts of acid produced in the various parts of the purifying plant:—

Source.	Per cent. H_2SO_4.	Per cent. of Total Production (5 tons).	Parts Arsenic per Million.
"Oxide" coolers . .	101·3	1·20	600
Main fan . . .	99·1	2·44	180
Acid catcher . .	95·9	1·39	...
["Platinum" cooler] .	105·1	0·09	45
Filters	...	No drip	...

The main fan eliminates nearly one-half of the mist, but this half is largely composed of coarser particles carried over from the second absorption tower. It is found, in fact, that the condensate in the fan is usually of nearly the same strength as the acid in this tower, and that its amount is proportional to the

tower feed. The acid catchers deal with the remainder of the coarser mist and the filters with the fine particles, but an amount which may vary considerably escapes from the filters and passes on. It is stated[1] that from 1·0 to 1·2 gm. per cubic metre usually pass from the fan to the acid catchers, from 50 to 100 mgm. from the catchers to the filters, and from 2 to 4 mgm. per cubic metre only should escape from the filters. These last figures might, perhaps, be obtained when the filters are newly packed, but the amount of mist passing to the rest of the plant is in general much higher. On one large plant,[2] the average of tests on eight sections (omitting abnormally high results) gave 0·026 gm. per cubic metre. The efficiency of the purification system, reckoned from percentages of mist entering and leaving, is often a high one; but, whether the amount which escapes is sufficient to carry arsenic in deleterious quantity, or whether arsenic passes through which mere filtration cannot affect, the fact remains that the removal of arsenic is incomplete, and more or less frequent renewal of the mats is necessary.

The efficiency of the oxide shafts as arsenic catchers has been variously estimated and, on a percentage basis, is higher the more arsenic the ore contains. It should be 90 per cent. or more for ores of medium arsenic content. On a pre-war unit, in 1909, burning 6 tons per day of Tharsis ore, the arsenic caught in the contact shafts was found to amount to 23·9 lb. per day. That trapped in the acid running from the fan, catchers, and filters was 0·16 lb. (as As); 1·7 mgm. per cubic metre left the filters in the gas, and 1·1 mgm. per cubic metre left the platinum contact shafts. Of the total amount leaving the burners (25·5 lb.), about 94 per cent. was therefore retained by the oxide and about 5 per cent. passed through all the purifying boxes.

In another series of tests made at Gretna in 1917, where 5½ tons of Peña ore (containing only 0·06 per cent. As) were being burnt per day, the percentage retained in the oxide shafts was only 63, but that passing from the filters in the gas (equal to 2 mgm. As per cubic metre) was 29 per cent. of the total issuing from the burners. Considerable evidence

[1] Parkes, *loc. cit.*
[2] *T.R.E.S.*, 1921, 5, 17.

was obtained to support, although not to establish, that the arsenic passes through in a volatile form generated by the action of iron on arsenical acid sludge. To the production of this gas the Mannheim plant, with coolers, pipes, and filters, all of cast-iron or steel, should appear to be particularly liable. In view of all these facts it is clearly of importance to select an ore containing as little arsenic as possible.

The purification system of the Mannheim plant is unequal to the demands made on it, and the ease in renewing the contact-mass is only a very partial compensation. Improvements in the system would necessarily follow rather novel lines. The air drying could hardly be given up without making the purification more difficult; the separate absorption of trioxide from the oxide shafts is a necessity, and these two conditions preclude any wet method of purification. For some other methods of arsenic removal Chapter VI. (p. 201) may be consulted.

The "Platinum" Conversion System.—The temperature in the platinum chest is regulated by two pyrometers, one in the superheater header from which the gas enters, and one in the outlet of the chest. These temperatures vary considerably according to the age of the plant and the condition of the platinised mats. With new mats, in a new plant, entry at 400° may give good conversion. A number of units which have been working for some time with a certain proportion of rewashed mats may show entry temperatures lying between 420° and 500°, and averaging about 460°. If a set of mats is continued in use unchanged it becomes necessary to raise the temperature more and more to obtain a conversion which is permissible, and when 500° or 510° has been reached it is usually found that conversion has sunk so much that a change of at least one element is advisable. The new element is put in at the top and the bottom one removed for washing, the original topmost element being reinserted in the middle. To carry out this removal, the element is pulled partially out by means of a hooked bar inserted in one of the handles of the upper frame, and is supported on trestles or on a long iron bar held with the point on the shelf of the chest. Grapples are then fitted (Fig. 133) and the element swung down to the floor level by a suitable tackle.

The temperature in the outlet will generally be 30° or 40°

higher than in the inlet, but the heat transference to or from the chest in its customary position is uncertain, and the indications of the outlet pyrometer have only a relative value. The gas entering the chest should average 3·0 per cent. of sulphur dioxide and 3·5 per cent. should not be exceeded. The percentage of oxygen should be about 12 to 12·5. These figures are checked daily by continuous gas tests made at the outlet from the filters, and the necessary alterations are best made by varying the speed of the main fan or blower. It has sometimes been found, however, that the sulphur dioxide in the gas leaving the filters cannot be reduced to 3 per cent. or so in this way without drawing more air through the burners than is advisable, and a vent in the main between the "oxide" coolers and the first absorption tower is therefore sometimes made, through which the necessary excess air can be drawn in without unduly cooling the burners and oxide shafts.

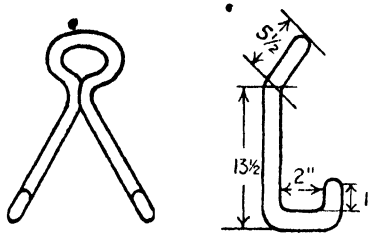


FIG. 133.

It is not easy to give representative figures for the "platinum" conversion because, like the necessary inlet temperature, this varies with the condition of the mats and the age of the plant. At first, with mats in good condition, about 90 per cent. should be obtained, and for a few months with careful working perhaps even 92 per cent.; but after this it is probable that the whole plant becomes more or less impregnated with arsenic and settles down to steady work, in which, with fairly frequent renewals of mats, between 80 and 86 per cent. may be obtained. After some years of operation of any unit, it is doubtful whether the platinum is ever free from arsenic; but this is not an insuperable disadvantage, for a considerable amount is necessary to cause conversion to sink below say 83 per cent., at the temperatures at which the mats are worked. Efficiency then becomes dependent mainly on the rewashing and renewal of the mats, both processes involving heavy losses of the platinum. The total amount of platinum, however, is relatively smaller than on any other plant.

The amount of arsenical material which can be present in mats which are still functioning fairly actively is surprisingly large. In one case of mats which had been ten weeks in use in 1912, 38 gm. of arsenic (As) were found to be associated with 100 gm. of platinum; others which had been used for six months contained 55 gm. for every 100 gm. of platinum. In a number of tests made on eight mats of one section of a unit the least quantity found per mat was 2·3 gm. in one of the newest; and the greatest 40·7, in one of the oldest. It is probable that the chemical and physical alteration of the asbestos, under the action of the hot sulphur trioxide, and the deposition of solid matter, have much to do with the loss of activity. The details given in the discussion of the methods for preliminary treatment of the mats, and for rewashing them, would tend to support this view (Chapter IV., part 2).

Absorption.—As the description of the absorption system of the Kynoch plant has already been made clear, the regulation of the system depends on the adjustment of a large number of valves. Practice is required to maintain the acid in the circulation tanks at the right strength, and to keep a fairly constant level of acid in all four tanks at once. With an overflow system the supervision is greatly simplified.

The main requirement in operating any Mannheim absorption system, beyond running off the proper strength of oleum, is to secure the best possible absorption in the two towers constituting the "oxide" absorption system. Any failure to do this results in either trioxide, or large quantities of acid mist, passing into the acid catchers. It is therefore necessary to have acid of 98 per cent. in the first circulation tank, and not to allow it to exceed this strength by more than, say, 0·5 per cent., for even under 100 per cent. the acid will fume seriously if the temperature be sufficiently high. The contents of No. 2 tank (tower 1) will be, usually, weak oleum of about 5 per cent., No. 3 tank will contain, say, 10 per cent. oleum, and No. 4, 20 per cent. The temperature in the tanks, with the usual cooling jackets, is usually from 50° to 60°, the gas entering the first tower at about the same temperature, and the third tower at 55° to 70°.

The jacketed reservoirs of the Kynoch plant were apt to give much trouble by springing leaks at the joints of the

outlet pipes passing through the jackets, and have been replaced, in later designs, by small cooling coils connected to the acid outlets of the first and third towers.

General Data.—In the table below are given a series of pressures and temperatures which are representative of those obtaining in a Kynoch plant in good order.[1] It is particularly necessary to keep records of pressures at various points and preferable to record them graphically. Any gradual increase of resistance at any point can then be detected, and a remedy applied. If this is neglected not only are blockages likely to occur, but the resistance of the plant as a whole may increase slowly, with serious results to its capacity. The data are supplementary to those already given.

Temperature and Pressure Data.

Point.	Temp. 0°C.	Press. ins. Water.	Point.	Temp. 0°C.	Press. ins. Water.
Leaving air fan	...	+1·8	Leaving filters	15	+2·4
„ air-drying tower	...	0·8	„ heat exchanger	240	...
„ "forewarmer" chamber	510	−0·2	„ "forewarmer" pipes	370	...
„ "oxide" coolers 1 and 2	159	...	„ superheater	480	...
„ "oxide" cooler 3	65	−1·1	„ platinum chest	500	...
„ absorption tower 1	45	−1·6	„ heat exchanger	230	...
„ „ „ 2	35	−2·0	„ "platinum" cooler	80	0·9
„ main fan	...	+3·0	„ absorption tower 3	60	0·6
„ acid catchers	...	+2·7	„ „ „ 5	...	0·1

Efficiency.—The overall efficiency of a Mannheim, as of any pyrites-burning plant, is the product of two factors, one representing the proportion of sulphur burnt, and the other the total ("oxide" and "platinum") conversion. It is calculated as usual from the known amounts of sulphur supplied and remaining in the burnt one, and the net amount of acid made. This calculation can be checked by comparison with the overall conversion of sulphur burnt, but this quantity is difficult to ascertain on a Mannheim plant, and is most readily and certainly found by the indirect method which has been given in Chapter V.

An overall efficiency of 85 per cent. would be counted a

[1] *T.R.E.S.*, 1921, 9, 24, 29.

good one, and although this figure has often been reached on runs of short period it has not usually been held for long. Of the plants erected during the War, that with the best record for its total period of running was the Oldbury installation of two units. The efficiency over a period of twenty months was 79·5 per cent.[1] This may be compared with the results of a run of two months with two units at Gretna in 1918, the main data of which are given below.

Pyrites charged (45·05 per cent. S)	= 847·1 tons
Equivalent SO_3	= 954·10 „
SO_3 produced	= 767·30 „
Residue (3·56 per cent. S)	= 676·8 „
SO_3 equivalent to S in residue	= 60·28 „

Efficiency on sulphur burnt = 85·85 per cent.
„ „ charged = 80·43 „ „

A large Mannheim installation burnt, during 1916, 9121 tons of Tharsis ore (50·43 per cent. S) and recovered 9364 tons of trioxide, the cinder containing 5·22 per cent. S (= 3·74 per cent. on the pyrites). From this:—

Efficiency on sulphur burnt = 87·9 per cent.
„ „ charged = 81·5 „ „

The comparatively low overall recovery effected by the Mannheim plant is only a partial objection, and might be counterbalanced by a low cost for labour and maintenance. But in general both these costs are high.[2] A redesign of the plant which removed the present weak features would no doubt to some extent lessen the cost of maintenance, but the remodelling would have to be drastic to affect seriously the high charge for labour. Hand-worked burners are costly to operate. They might be replaced by Herreshofs entirely if the difficulty of obtaining gas hot enough to enter the contact shafts could be overcome without using lump burners to supply additional heat. The filling of the oxide shafts necessitates also a considerable amount of labour, not to mention the frequent repacking of a number of small filters, and the removal and insertion of contact-elements.

The Mannheim plant as a whole, however, in spite of many

[1] *Second Report on Costs of H.M. Factories*, p. 28.
[2] See *Second Report of Costs and Efficiencies of H.M. Factories*, 1918.

disadvantages, presents some attractive features. It is not expensive to instal. The units are suitable to a small production, and the amount of platinum is much less than in any other plant. It is possible that a new type of plant depending on the same principle of employing ferric oxide on some other cheap catalyst in addition to platinum, may in time be evolved. Such a plant would have mechanical burners only; the purification system would be larger and more efficient than the present one; the contact-chamber would be removed from its present position and made more accessible and capable of better regulation of temperature; the superheater would be remodelled, and for ordinary running, dispensed with altogether; and the absorption system would be simplified and reduced in bulk. It is possible that Grillo contact-mass could replace asbestos with advantage, being introduced in trays similar in shape to the present elements. Without some such radical alterations in design, the future of the Mannheim process is by no means assured.

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